

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-090637

(43)Date of publication of application : 04.04.1997

(51)Int.Cl.

G03F 7/039

G03F 7/004

G03F 7/30

H01L 21/027

BEST AVAILABLE COPY

(21)Application number : 07-312722

(71)Applicant : FUJITSU LTD

(22)Date of filing : 30.11.1995

(72)Inventor : NOZAKI KOJI

YANO EI

WATABE KEIJI

NAMIKI TAKAHISA

IGARASHI YOSHIKAZU

KURAMITSU YOKO

TAKECHI SATOSHI

KODACHI AKIKO

TAKAHASHI MAKOTO

(30)Priority

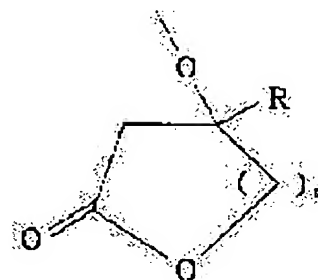
Priority number : 07178717 Priority date : 14.07.1995 Priority country : JP

(54) RESIST COMPOSITION AND RESIST PATTERN FORMING METHOD

(57)Abstract:

PROBLEM TO BE SOLVED: To obtain a resist compsn. having a sensitivity capable of practical use and capable of forming a nonswellable fine resist pattern.

SOLUTION: An acid-sensitive polymer contained in this chemical amplification type resist compsn. in combination with an optical acid generating agent contains a lactone part represented by the formula [where R is optionally subst'd. 1-4C straight chain or branched chain alkyl and (n) is an integer of 1-4] as a protective group for each carboxyl group.



LEGAL STATUS

[Date of request for examination]

24.03.2000

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

3297272

[Date of registration]

12.04.2002

▶▶
[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

* NOTICES *

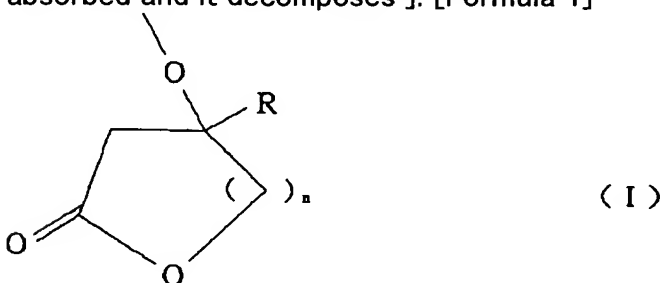
JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] It is the film-forming polymer which has a protective group content carboxyl group in the side chain of a monomeric unit. The acid sensitivity polymer which can become meltable in a basic water solution when it is insoluble in a the very thing basicity water solution, however the protective group of said carboxyl group is desorbed from a side chain, The lactone part with which said acid sensitivity polymer is expressed by the degree type (I) in that case coming [the photo-oxide generating agent which can generate the acid with which the desorption of the protective group of said carboxyl group can be caused if the radiation for image formation is absorbed and it decomposes]: [Formula 1]



It is the resist constituent which is characterized by containing (R may express the alkyl group of the straight chain which has 1-4 carbon atoms, or branched chain, and you may be a permutation or unsubstituted any, and n is the integer of 1-4 in an upper type) as a protective group of said carboxyl group and in which development with a basic water solution is possible.

[Claim 2] The resist constituent according to claim 1 characterized by guiding said lactone part from (**) - mevalonic lactone.

[Claim 3] The resist constituent according to claim 1 or 2 characterized by being 1 member chosen from the group which a polymerization partner's monomeric unit in said acid sensitivity polymer becomes from the monomeric unit which has an ester group containing the alicyclic hydrocarbon part of an acrylate (meta) system monomeric unit, a vinyl phenol system monomeric unit, N-permutation maleimide system monomeric unit, a styrene system monomeric unit and plurality, or a polycyclic type.

[Claim 4] the resist constituent according to claim 3 with which the alicyclic hydrocarbon part of said monomeric unit is characterized by being an adamantyl radical and (or) a norbornyl radical.

[Claim 5] It gives a quartz substrate and is 1 micrometer of thickness on the substrate. Resist constituent given in any 1 term of claims 1-4 characterized by the transmission in the wavelength (180-300nm) of the exposure light source of deep ultra-violet range being 30% or more when a coat is formed.

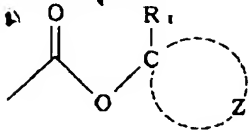
[Claim 6] The part as which a polymerization partner's monomeric unit in said acid sensitivity polymer has a carboxyl group containing the protective group from which it can be desorbed according to an operation of the additional acid from said photo-oxide generating agent in the side chain of the monomeric unit, and is expressed in it by the degree type (II) in that case: [Formula 2]



It is the resist constituent according to claim 1 or 2 characterized by containing (R1 expresses the alkyl group of the straight chain which has 1-4 carbon atoms, or branched chain, you may be a permutation or unsubstituted any, and Z expresses two or more atoms required to complete an alicyclic hydrocarbon radical with the carbon atom which R1 combined in an upper type) as a protective group of said carboxyl group.

[Claim 7] The resist constituent according to claim 6 with which the above mentioned additional protective group content carboxyl group is characterized by what is expressed by the degree type (III).

[Formula 3]



... (111)

(In an upper type, R1 and Z are the same as said definition respectively) .

[Claim 8] A resist constituent given in any 1 term of claims 1-7 characterized by being the form of the solution which dissolved in the solvent chosen from the group which consists of ethyl lactate, methyl amyl ketone, methyl-3-methoxy propionate, ethyl-3-ethoxy propionate, propylene glycol methyl ether acetate, and its mixture.

[Claim 9] The resist constituent according to claim 8 characterized by including further the solvent chosen from the group which consists of butyl acetate, gamma-butyrolactone, propylene glycol methyl ether, and its mixture as an auxiliary solvent.

[Claim 10] The following process: The formation approach of a resist pattern characterized by coming to contain developing the resist film after exposure in a basic water solution by applying a resist constituent given in any 1 term of claims 1-9 on a processed substrate, and exposing the formed resist film alternatively with the radiation for image formation which can carry out induction of the decomposition of the photo-oxide generating agent of said resist constituent.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] When this invention is described in more detail about a resist constituent, it relates to a resist constituent like excimer laser which can use the light of short wavelength as a radiation for image formation more, and can develop negatives with a basic water solution after exposure. This invention relates to the formation approach of the positive type resist pattern which used such a resist constituent again. The resist constituent of this invention belongs under the category of the so-called "chemistry magnification mold resist", is usable sensibility and can form a detailed positive pattern without swelling.

[0002]

[Description of the Prior Art] In recent years, high integration progresses, as for the semiconductor integrated circuit, LSI and VLSI are put in practical use, and the minimum line width of a circuit pattern has reached the field of a subhalf micron. For this reason, it is indispensable to establish ultra-fine processing technology, in the lithography field, as a solution of that demand, the wavelength of the ultraviolet rays of the exposure light source is made to shift to the short wavelength of a far-ultraviolet field, and development of the aligner using the light source of the wavelength of deep ultra-violet range also prospers further. In connection with this, a resist ingredient also has more little absorption of light in the above short wavelength, and development of the ingredient which doubles and has dry etching resistance with sensibility high good serves as pressing need.

[0003] Development of the resist which the photolithography using krypton fluoride excimer laser (it omits the wavelength of 248nm and Following KrF) as a new exposure technique in current and semi-conductor manufacture is studied briskly, and gave good sensibility and definition in such a short wavelength field, and has stability is becoming pressing need. As a resist with the high sensitivity and high resolution which can respond to such a source of short wave Nagamitsu The resist constituent using the concept called a chemistry magnification mold is already presented by H.Ito and others of U.S. IBM. for example, J.M.J.Frechet et al. and Proc.Microcircuit Eng. -- 260 (1982), H.Ito et al., Digest of Technical Papers of 1982 Symposium on VLSI Technology, 86 (1983), H.Ito et al., "Polymers in Electronics", ACS Symposium Series Please refer to the volume 242 and on T.Davidson, ACS, 11 (1984), and U.S. Pat. No. 4,491,628. The fundamental concept of the above-mentioned resist constituent makes catalytic reaction cause in the resist film, raises an apparent quantum yield, and, therefore, is based on attaining high sensitivity-ization of the resist constituent so that I may be easily understood from the above-mentioned reference etc.

[0004] If the chemistry magnification mold resist which be widely study by the current emergency and which added the photo-oxide generating agent (PAG) which have the operation which generate an acid by light to the t-butoxy KARUBONIRUPORI vinyl phenol (t-BOCPVP) be take for an example, in the exposure section of a resist, by heating after exposure, and the so-called "the PEB (postexposure baking)", a t-BOC radical will **** and it will become isobutene and a carbon dioxide. Moreover, the proton acid produced at the time of desorption of t-BOC serves as a catalyst, the above-mentioned deprotection reaction advances continuously, and the polarity of the exposure section changes a lot. In the resist of this example, a resist pattern can be easily formed by choosing the suitable developer which can respond to a big change of the polarity of the exposure section.

[0005] However, since the chemical structure of the resin has constraint, the conventional chemistry magnification mold resist has the problem that it is difficult to satisfy all requirements, such as sensibility, transparency in exposure wavelength, preservation stability, the ease of acquisition, and definition. Especially an important point is constraint of the protective group from which it should be desorbed by heat-treatment under existence of the photo-oxide generating agent in a chemistry magnification mold resist. namely, when the chemistry magnification intervention component which exists in the side chain of the monomeric unit of a film-forming polymer is carboxylate, as for the suitable protective group for the carboxyl group, t-butyl, 1, and 1-dimethylbenzyl radical, a tetrahydropyranyl group, a 3-oxocyclohexyl radical, an isobornyl radical, etc. are known -- **** -- it does not pass but to offer still more effectively the protective group which can act is desired.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to be able to follow, to be able to

solve a trouble of a Prior art which was described above, able to use a basic water solution as a developer, have usable sensibility, and offer the new resist constituent which can form a detailed pattern without swelling.

[0007] The purpose of this invention can respond also to the exposure light source of deep ultra-violet range, such as KrF excimer laser, and is again to offer the new resist constituent excellent also in dry etching resistance. Another purpose of this invention is to enlarge the polarity between the exposure section and the unexposed section, and offer the new resist constituent which can form high sensitivity, and high contrast and the pattern which follows and has high resolution.

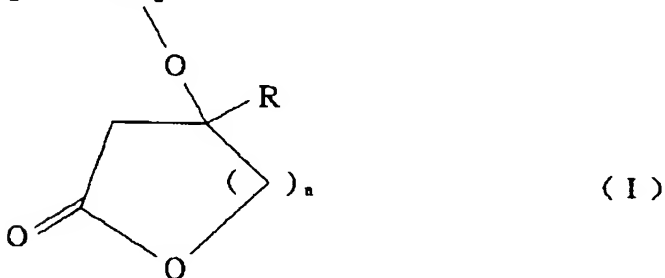
[0008] One purpose is now [of this invention] to offer the approach of forming a resist pattern using such a new resist constituent.

[0009]

[Means for Solving the Problem] That the above-mentioned technical problem should be solved, wholeheartedly, as a result of research, this invention persons acquire the knowledge that it is effective to use what uses the film-forming polymer which has a protective group content carboxyl group for the side chain of a monomeric unit as a polymer used as base material resin in a chemistry magnification mold resist constituent, and has a specific lactone part as a protective group of the carboxyl group of the polymer, and came to complete this invention.

[0010] This invention is a film-forming polymer which has a protective group content carboxyl group in the side chain of a monomeric unit in the one field. The acid sensitivity polymer which can become meltable in a basic water solution when it is insoluble in a the very thing basicity water solution, however the protective group of said carboxyl group is desorbed from a side chain, Lactone part with which said acid sensitivity polymer is expressed by the degree type (I) in that case coming [the photo-oxide generating agent which can generate the acid with which the desorption of the protective group of said carboxyl group can be caused if the radiation for image formation is absorbed and it decomposes] : [0011]

[Formula 4]

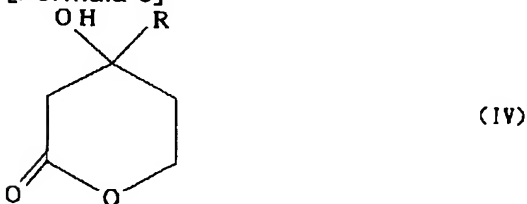


[0012] It is in the resist constituent in which development is possible in the basic water solution characterized by containing (R may express the alkyl group of the straight chain which has 1-4 carbon atoms, or branched chain, for example, a methyl group, an ethyl group, a propyl group, etc., and these radicals may be a permutation or unsubstituted any, and n is the integer of 1-4 in an upper type) as a protective group of said carboxyl group.

[0013] In the resist constituent by this invention, the acid sensitivity polymer used as the base material resin includes the various polymers from the homopolymer which is used in large semantics, therefore consists only of a single monomeric unit to the copolymer (a 3 component copolymer etc. is included) of such a monomeric unit and the monomeric unit of others of arbitration. at least one of the monomeric units from which the polymer used here constitutes it preferably -- and When the polymer takes the form of a copolymer especially, the monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group An acrylate system monomeric unit, i.e., an acrylate system, and a methacrylate system monomeric unit, (Meta) A vinyl phenol system monomeric unit, N-permutation maleimide system monomeric unit, It is what is the monomeric unit which has an ester group containing the alicyclic hydrocarbon part of a styrene system monomeric unit, plurality, or a polycyclic type. Still more preferably an alicyclic hydrocarbon part is the monomeric unit which has the ester group containing the alicyclic hydrocarbon part of the plurality which is an adamantyl radical and (or) a norbornyl radical, or a polycyclic type.

[0014] Moreover, the lactone part as a protective group of the carboxyl group contained in the side chain in this acid sensitivity polymer is (**)--mevalonic lactone: [0015] preferably expressed by the degree type (IV) although it is said that it can have the structure of arbitration.

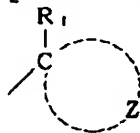
[Formula 5]



[0016] It is guided from (the inside of a formula and R are the same as said definition). The resist constituent of

this invention gives it to a quartz substrate, and is 1 micrometer of thickness on the substrate further again. When a coat is formed, the permeability in the wavelength (180–300nm) of the exposure light source of deep ultra-violet range is 30% or more preferably. When the above mentioned acid sensitivity polymer takes the gestalt of a copolymer, having the additional protective group content carboxyl group also has the desirable monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group. namely, the monomeric unit containing the 1st protective group content carboxyl group in which an acid sensitivity copolymer contains said lactone part carried out as a protective group -- in addition, you may have the monomeric unit containing the 2nd protective group content carboxyl group, and such a combination is also desirable. Here, the monomeric unit containing the 2nd protective group content carboxyl group is partial: [0017] which has a carboxyl group containing the protective group from which it can be desorbed according to an operation of the additional acid from said photo-oxide generating agent in the side chain of the monomeric unit, and is preferably expressed with it by the degree type (II) in that case.

[Formula 6]



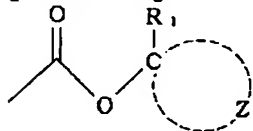
... (II)

[0018] It is the monomeric unit which contains (R1 expresses the alkyl group of the straight chain which has 1–4 carbon atoms, or branched chain, you may be a permutation or unsubstituted any, and Z expresses two or more atoms required to complete an alicyclic hydrocarbon radical with the carbon atom which R1 combined in an upper type) as a protective group of said carboxyl group.

[0019] Although it is said with various gestalten that the 2nd protective group content carboxyl group may exist, it is preferably expressed by the degree type (III).

[0020]

[Formula 7]



... (III)

[0021] (In an upper type, R1 and Z are the same as said definition respectively) . The resist constituent of this invention is offered in the form of the solution which dissolved in the solvent preferably chosen from the group which consists of ethyl lactate, methyl amyl ketone, methyl-3-methoxy propionate, ethyl-3-ethoxy propionate, propylene glycol methyl ether acetate, and its mixture. Moreover, this resist solution may contain further the solvent chosen from the group which consists of butyl acetate, gamma-butyrolactone, propylene glycol methyl ether, and its mixture as an auxiliary solvent if needed.

[0022] Moreover, this invention is the approach of forming a resist pattern in the field of another, applies the following resist constituent of process: this invention on a processed substrate, and exposes the formed resist film alternatively with the radiation for image formation which can carry out induction of the decomposition of the photo-oxide generating agent of said resist constituent, and is in the formation approach of the resist pattern characterized by coming to contain developing the resist film after exposure in a basic water solution.

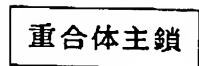
[0023] As for the resist film formed on the processed substrate, in the formation approach of the resist pattern by this invention, it is desirable to present heat-treatment after that, before presenting a selection exposure process with it. That is, by this invention approach, while presenting prebaking processing before the exposure, before developing negatives by being after exposure, postbake processing in which it explained as PEB (postexposure baking) previously is presented with the resist film. These heat-treatment can be advantageously carried out according to a conventional method.

[0024]

[Embodiment of the Invention] The formation approach of the resist constituent by this invention and a resist pattern can be enforced with various desirable gestalten so that he can understand easily from the following detailed explanation. This invention relates to the resist constituent of the chemistry magnification mold in which development is possible with the basic water solution for forming a positive resist pattern on a processed substrate. This resist constituent is a film-forming polymer which has a protective group content carboxyl group in the side chain of the (a) monomeric unit, as described above. The acid sensitivity polymer which can become meltable in a basic water solution when it is insoluble in a the very thing basicity water solution, however the protective group of said carboxyl group is desorbed from a side chain, (b) It comes to contain the photo-oxide generating agent (PAG) which can generate the acid with which the desorption of the protective group of said carboxyl group can be caused if the radiation for image formation is absorbed and it decomposes. Moreover, said acid sensitivity polymer contains the specific lactone part with which it is expressed by the front type (I) as a

[0025]

手合仕立



[0027] Moreover, especially the acid sensitivity polymer used as base material resin in the resist constituent of this invention can be set when it takes the gestalt of a copolymer, and in addition to having easily the functional group from which it can be desorbed with heating under existence of an acid catalyst, also in the 2nd monomeric unit, it can have the same functional group into the ester part of the 1st monomeric unit. In such a case, since the functional group of both in a copolymer may **** by the acid catalyzed reaction, sensibility and definition higher than the copolymer constituted so that the functional group of one of the two's monomeric unit might **** and a soluble change might be given can be reconciled.

[0029] moreover, in using the exposure light source of an ultrashort wavelength field like argon fluoride (ArF) excimer laser Since the transparency in the wavelength (193nm) of the exposure light source concerned is needed with dry etching resistance, It is the polymer which was described above and the strong aromatic series ring of absorption is not included. Instead Use of the polymer and division acrylate system which have the ester

group which dry etching resistance is high, for example, contains the alicyclic hydrocarbon part of the plurality or polycyclic type represented by an adamantyl radical and the norbornyl radical, and a methacrylate system polymer is recommended. Here, the alicyclic hydrocarbon part which should be contained in an ester group includes well-known various radicals in the field of a chemistry magnification mold resist. If a suitable alicyclic hydrocarbon radical shows the example, it will make the following compounds a frame.

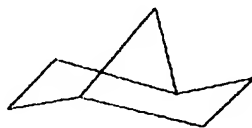
[0030] (1) Adamantane And the derivative (2) norbornane And the derivative (3) par hydronalium anthracene And the derivative (4) par hydronalium naphthalene and derivative (5) tricyclo -- [-- 5.2.1.02, 6] Deccan, its derivative (6) bicyclo hexane, its derivative (7) spiro [4, 4] nonane, derivative (8) spiro [4, 5] Deccan, and its derivative -- the compound of these, respectively : expressed with the following structure expressions [0031]

[Formula 9]

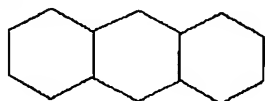
(1)



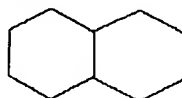
(2)



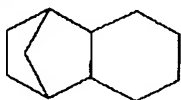
(3)



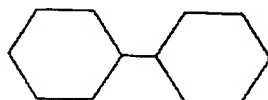
(4)



(5)



(6)



(7)



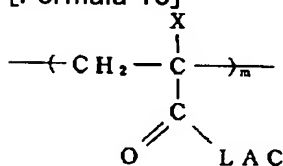
(8)



[0032] Furthermore, the molecular weight (weight average molecular weight and Mw) of an acrylate system polymer (meta) which was described above, and other acid sensitivity polymers can be changed in the large range. Preferably, the range of the molecular weight of this polymer is 2000-1 million, and its range of 3000-50000 is more desirable. Although the acid sensitivity polymer which can be advantageously used in operation of this invention is not necessarily still more specifically limited to what is enumerated below, it includes the following polymers. In addition, m in a formula is the number of monomeric units (repeat unit) required to obtain the above-mentioned weight average molecular weight, and LAC expresses the lactone part of a front type (I), and they are cyano groups, such as low-grade alkyl groups, for example, a methyl group etc., such as the substituent of arbitration, for example, a hydrogen atom, a halogen atom, for example, chlorine, and a bromine, and others except for the case where X has a notice especially.

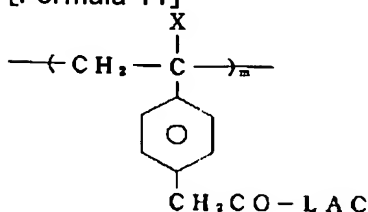
(1) (meta) Acrylate system polymer [0033]

[Formula 10]



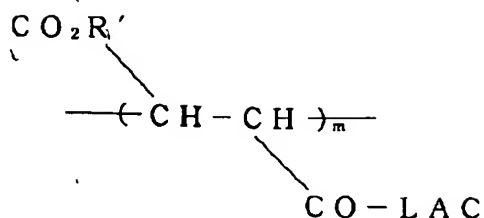
[0034] (2) Vinyl phenol system polymer [0035]

[Formula 11]



[0036] (3) Fumaric-acid system polymer [0037]

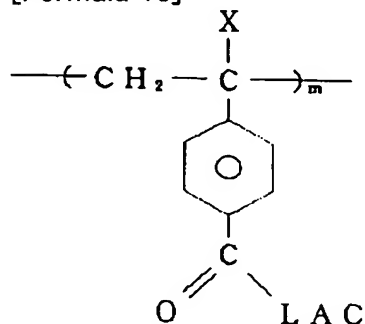
[Formula 12]



[0038] In an upper type, R' expresses said LAC or expresses others for aryloxy groups, for example, a phenoxy group, such as an alkoxy group, for example, a methoxy group, an isopropoxy group, and a t-butoxy radical, a benzyloxy radical, etc.

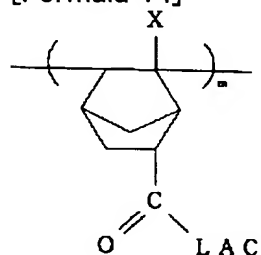
(4) Vinyl benzoic-acid system polymer [0039]

[Formula 13]



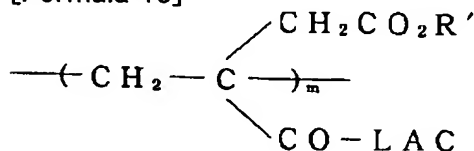
[0040] (5) Norbornene carboxylic-acid system polymer [0041]

[Formula 14]



[0042] (6) Itaconic-acid system polymer [0043]

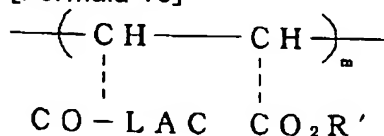
[Formula 15]



[0044] In an upper type, R' is the same as said definition.

(7) Maleic-acid system polymer [0045]

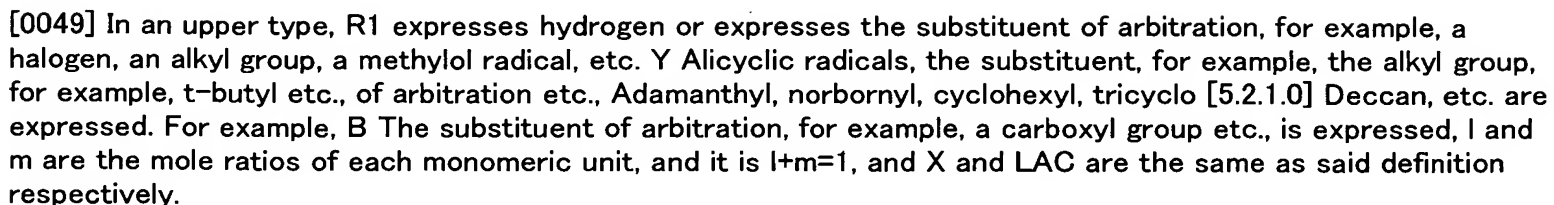
[Formula 16]



[0046] In an upper type, R' is the same as said definition. in addition, also in advance, these polymers were explained -- as -- suitable other monomeric units and ***** -- the copolymers (a 2 component copolymer, 3 component copolymer, etc.) of arbitration may be constituted. The acid sensitivity copolymer which can be used in this invention is as being shown in the following formula (V) and (VI), when the aforementioned (meta) acrylate system polymer is explained with reference to what is made into a subject. In addition, an acrylate (meta) system 3 component copolymer can also be constituted according to this.

[0047]

[Formula 17]

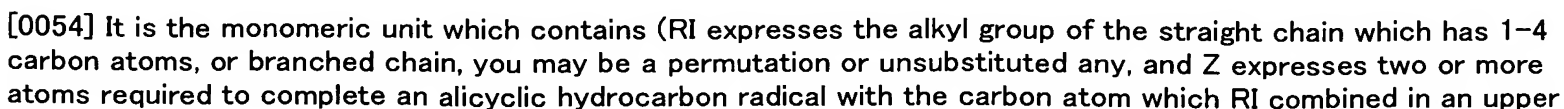


[0050] Moreover, if it clarifies in relation to this, the acrylate system polymer with which the usefulness was found out especially in this invention persons and which contains (**)—mevalonic lactone (meta) acrylic ester in a constituent (meta) is new, and is not taught at all by the Prior art. It can reach and other acrylate (meta) system polymers can be prepared using the polymerization method generally used in the chemistry of a polymer also including these things in the gestalt of a copolymer. For example, the acrylate (meta) system polymer of this invention can be advantageously prepared by carrying out the free radical polymerization of the predetermined monomer component in existence of the 2,2'-azobis isobutyronitrile (azobisuisobutironitoriru) as a free radical initiator, although detailed explanation is omitted in this application specification. Moreover, acid sensitivity polymers other than an acrylate (meta) system polymer can be similarly prepared advantageously according to a conventional method.

[0051] By the way, when an acid sensitivity polymer takes the gestalt of a copolymer, the rate of a monomeric unit of having the lactone part of a formula (I) in an ester group before occupying in the copolymer is 20 – 70 % of the weight preferably. If the content of this monomeric unit is less than 20 % of the weight, satisfying patterning will become impossible, and if it exceeds 70 % of the weight reversely [that], it will change to a basic water solution possible [the dissolution]. The content of this monomeric unit is 30 – 60 % of the weight still more preferably.

[0052] Moreover, when the acid sensitivity polymer contained as base material resin in it takes the gestalt of a copolymer in the resist constituent of this invention according to this invention persons' further knowledge, having the additional protective group content carboxyl group, as described above also has the desirable monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group. namely, the monomeric unit containing the 1st protective group content carboxyl group in which an acid sensitivity copolymer contains said lactone part carried out as a protective group -- in addition, you may have the monomeric unit containing the 2nd protective group content carboxyl group, and such a combination is desirable. Here, the monomeric unit containing the 2nd protective group content carboxyl group is partial: [0053] which has a carboxyl group containing the protective group from which it can be desorbed according to an operation of the additional acid from said photo-oxide generating agent in the side chain of the monomeric unit, and is preferably expressed with it by the degree type (II) in that case.

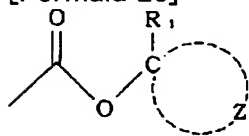
[Formula 19]



type) as a protective group of said carboxyl group. Although it is said with various gestalten that the 2nd protective group content carboxyl group may exist, it is preferably expressed by the degree type (III).

[0055]

[Formula 20]

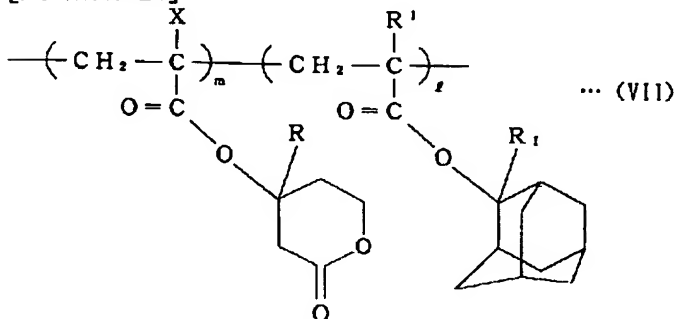


... (III)

[0056] It sets at an upper ceremony and is R1. And Z is the same as said definition respectively. When it states in more detail, the acid sensitivity copolymer which each monomeric unit has the protective group content carboxyl group, and can use advantageously in operation of this invention is a copolymer expressed by the degree type (VII) preferably.

[0057]

[Formula 21]

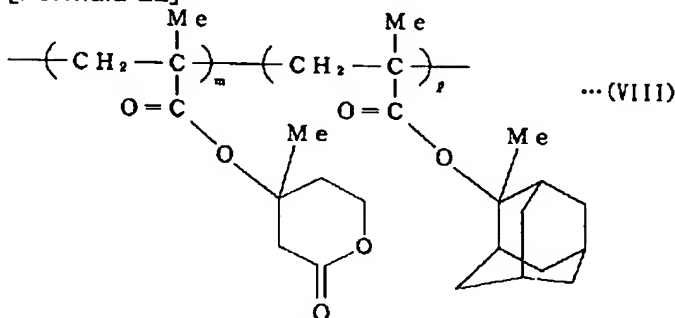


... (VII)

[0058] in an upper type, R, R1, and R1, X, m and l are the same as said definition respectively, and the substituents R1 and X combined with the carbon atom of a principal chain are the same -- or you may differ and they are a hydrogen atom or a low-grade alkyl group, for example, a methyl group, preferably. The acid sensitivity copolymer which can be used still more advantageous in operation of this invention is a methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamantyl copolymer which follows and is expressed by the degree type (VIII).

[0059]

[Formula 22]



... (VIII)

[0060] In an upper type, Me could express the methyl group, this methyl group may be replaced with the hydrogen atom, and m and l are the same as said definition respectively. In such a copolymer and the other same copolymers, since an adamantyl radical is included in the ester section, high dry etching resistance (RIE resistance) can be acquired. If it is going to acquire the RIE resistance of the novolak resist average by which the current general purpose is carried out here, it is required to make into about 50 mol % the content of the methacrylic-acid 2-methyl-2-adamantyl which is the 2nd monomeric unit in a copolymer. Moreover, since this copolymer has the structure which does not contain the strong aromatic series ring of absorption, it is very advantageous about the transparency in ultrashort wavelength (193nm) like argon fluoride (ArF) excimer laser.

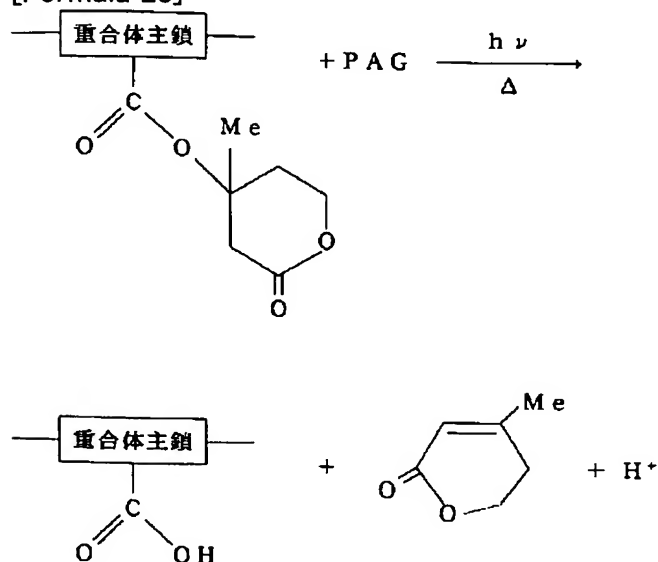
[0061] It is desirable still more desirable that it is generally about 20 - 70 % of the weight, and the content of the methacrylic-acid (**)-mevalonic lactone ester which is the 1st monomeric unit in a copolymer which was described above is about 30 - 60 % of the weight. Moreover, it is desirable still more desirable that it is generally about 20 - 80 % of the weight, and the content of the methacrylic-acid 2-methyl-2-adamantyl which is the 2nd monomeric unit in this copolymer is about 30 - 70 % of the weight. As it already explained that it was little or more abundant than range which each monomeric unit described above, and was contained, un-arranging [of changing to the basic water solution whose satisfying patterning becomes impossible possible / the dissolution] occurs.

[0062] Moreover, a similar reaction [in / the mechanism of the chemistry magnification in a copolymer including the 1st and 2nd monomeric units which were described above is the same as the mechanism of the chemistry magnification in the homopolymer explained previously fundamentally, and / the 2nd monomeric unit] will be added to this. Namely, it is known well that the polymer of an acrylic acid or a methacrylic acid has high transparency by deep ultra-violet range. Moreover, for example, the methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamantyl copolymer expressed by the before type (VIII) Since two kinds of ester sections contained do not contain a chromophore with a big molar extinction coefficient in 190-250nm in the structure, respectively It becomes the high sensitivity resist which will generate an acid if the radiation for image formation of optimum dose is absorbed and it decomposes, and can respond also to the exposure using deep ultraviolet advantageously if the compound (PAG) from which the above-mentioned ester section may be desorbed is combined.

[0063] If PAG is exposed to the radiation for image formation after formation of the resist film, it will absorb the radiation and will generate an acid. Subsequently, if the resist film after this exposure is heated, the acid produced previously will act in catalyst and the following reactions will advance to coincidence separately in the membranous exposure section.

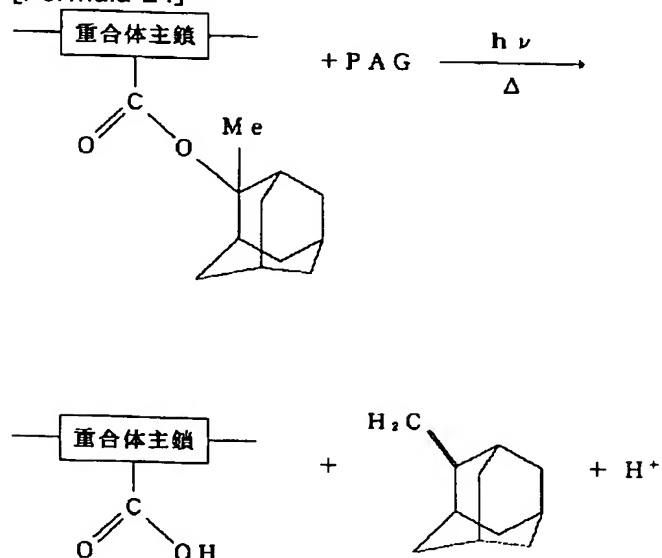
[0064]

[Formula 23]



[0065]

[Formula 24]

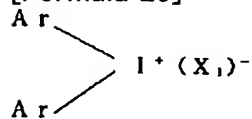


[0066] In a copolymer which was described above, since the functional group from which it can be desorbed is easily introduced into the ester part of the monomeric unit with heating under existence of an acid catalyst, by the desorption, proton acid can be reproduced and, therefore, high sensitivity can be attained. Moreover, since a carboxylic acid generates after desorption of a functional group, the exposure section of the resist film becomes meltable to a base, and, therefore, can be developed in a basic water solution. Since the exposure section carries out dissolution removal, the resist pattern obtained is a positive pattern. In this case, since pattern

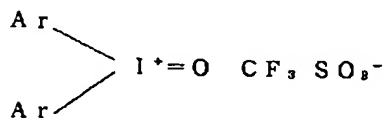
formation is performed using a polar change produced in a polymer, a pattern without swelling is obtained.
 [0067] Moreover, the photo-oxide generating agent (PAG) used combining an acid sensitivity polymer which was described above in the chemistry magnification mold resist of this invention can be matter which produces proton acid by the exposure of radiations, such as the photo-oxide generating agent generally used in the chemistry of a resist, i.e., ultraviolet rays, far ultraviolet rays, vacuum ultraviolet radiation, an electron ray, an X-ray, and a laser beam. The following is included although a suitable photo-oxide generating agent is not limited to what is enumerated below in operation of this invention.

(1) Iodonium salt expressed by the degree type : [0068]

[Formula 25]



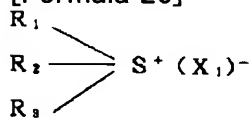
又は



[0069] (In an upper type, Ar expresses alicyclic or radicals, such as a phenyl group permuted by a permutation or an unsubstituted aromatic series radical, for example, a phenyl group, the halogen, the methyl group, t-butyl, an aryl group, etc., and X1 expresses BF₄, BF₆, PF₆, AsF₆, SbF₆, CF₃SO₃, ClO₄, etc.)

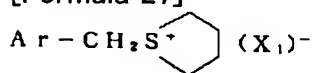
(2) Sulfonium salt expressed by the degree type : [0070]

[Formula 26]



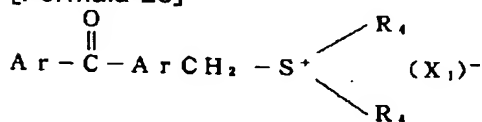
[0071]

[Formula 27]



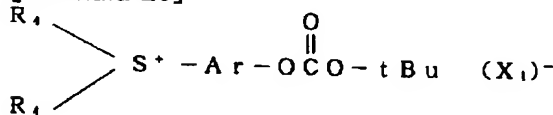
[0072]

[Formula 28]



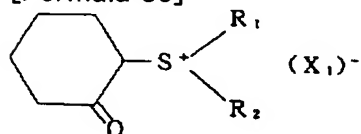
[0073]

[Formula 29]



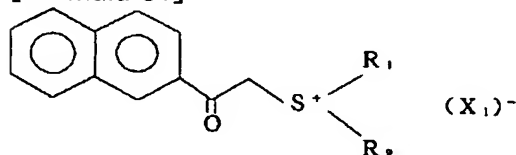
[0074]

[Formula 30]



[0075]

[Formula 31]



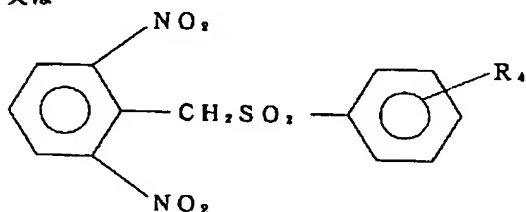
[0076] (In an upper type, R1, R2, R3, and R4 are the same -- or you may differ, and, respectively hydrogen is expressed, the substituent of arbitration, for example, a halogen, an alkyl group, an aryl group, etc. are expressed, R1, R2, and R3 are phenyl groups etc., R4 is a methyl group etc., and Ar and X1 are the same as said definition respectively)

(3) Sulfonate expressed by the degree type : [0077]

[Formula 32]



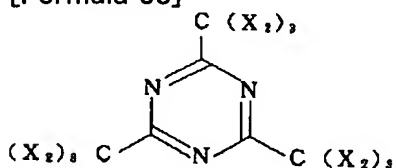
又は



[0078] (In an upper type, Ar and R4 are the same as said definition)

(4) OKISA azole derivative expressed by the degree type : [0079]

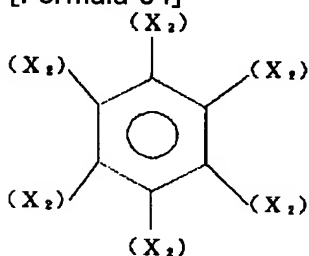
[Formula 33]



[0080] (In an upper type, X2 is a halogen, for example, Cl and Br, or I, however it is -CX3 One of the radicals may be a permutation, an unsubstituted aryl group, or an alkenyl radical)

(5) Halogenide expressed by the degree type : [0081]

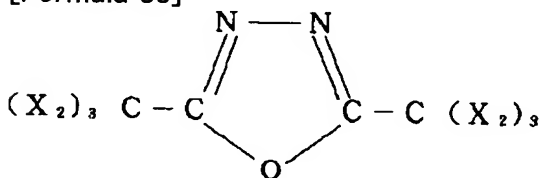
[Formula 34]



[0082] (In an upper type, X2 is the same as said definition)

(6) s-triazine derivative expressed by the degree type : [0083]

[Formula 35]

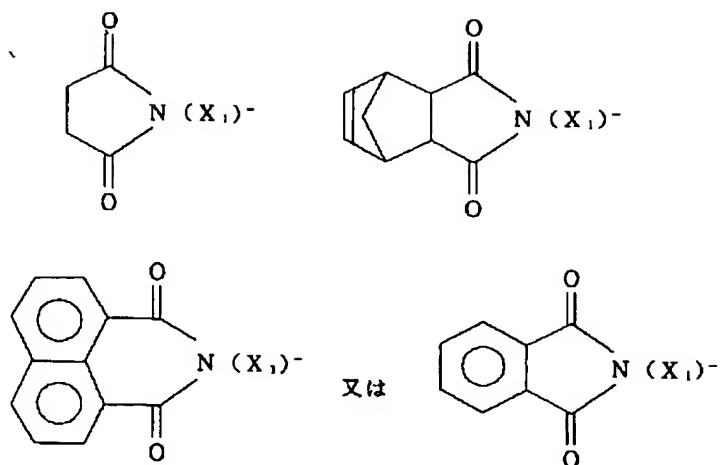


[0084] (In an upper type, X2 is a halogen, for example, Cl and Br, or I, however it is -CX3 One of the radicals may be a permutation, an unsubstituted aryl group, or an alkenyl radical)

(7) Disulfon derivative: $\text{Ar}-\text{SO}_2-\text{SO}_2-\text{Ar}$ expressed by the degree type (in an upper type, Ar is the same as said definition)

(8) Imide compound expressed by the degree type : [0085]

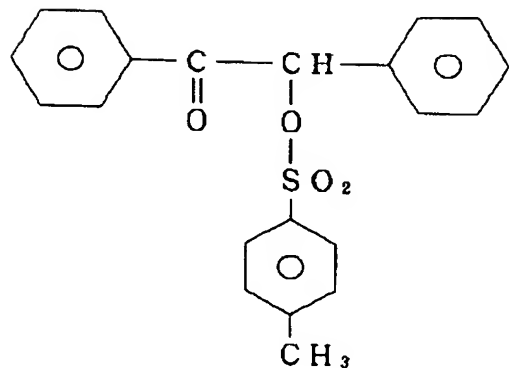
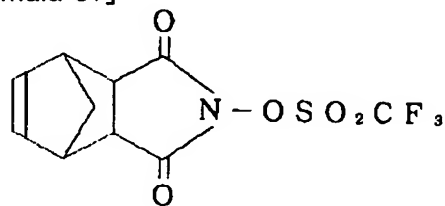
[Formula 36]



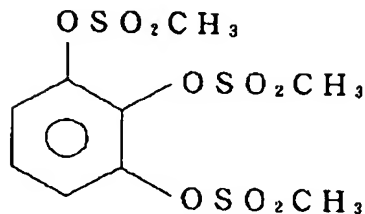
[0086] (In an upper type, X1 is the same as said definition)

(9) In addition, (the sulfonates expressed by the degree type) : [0087]

[Formula 37]



又は



[0088] These photo-oxide generating agents can be used in various amount into the resist constituent of this invention. According to this invention persons' knowledge, the amount of the photo-oxide generating agent used is 0.1 - 50 % of the weight on the basis of the whole quantity of a polymer preferably. When the amount of this photo-oxide generating agent exceeds 50 % of the weight, it becomes impossible to already perform patterning as a result of light being absorbed too much. The amount of the photo-oxide generating agent used is 1 - 15 % of the weight on the basis of the whole quantity of a polymer still more preferably.

[0089] Moreover, it is desirable to take into consideration the structure of a polymer and a photo-oxide generating agent and the amount of the photo-oxide generating agent used so that the transmission (value when forming the resist coat of 1 micrometer of thickness on a quartz substrate) in the exposure wavelength of the resist constituent of this invention which consists of an acid sensitivity polymer and a photo-oxide generating agent may become 30% or more in relation to the above. The resist constituent of this invention can be dissolved in a suitable organic solvent, and the above-mentioned acid sensitivity polymer and the above-

mentioned photo-oxide generating agent can usually be advantageously used for it in the form of a resist solution. An organic solvent useful to preparation of a resist solution is not limited to these, although ethyl lactate, methyl amyl ketone, methyl-3-methoxy propionate, ethyl-3-ethoxy propionate, propylene glycol methyl ether acetate, etc. are recommended. Although these solvents may be used independently, two or more kinds of solvents may be mixed and used for them if needed. Although especially the amount of these solvents used is not limited, it is desirable to use it in sufficient amount to obtain the suitable viscosity for spreading of spin spreading etc. and desired resist thickness.

[0090] In addition to a solvent (it is called especially the main solvent) which was described above, with the resist solution of this invention, an auxiliary solvent may be used if needed. Although use of an auxiliary solvent is unnecessary, when a solute with low solubility is used depending on the solubility of a solute, it is 10 ~ 20 % of the weight usually preferably [adding in 1 ~ 30% of the weight of an amount to the main solvent], and more preferably. Although the example of a useful auxiliary solvent is not limited to what also enumerates these below, it includes butyl acetate, gamma-butyrolactone, propylene glycol methyl ether, etc.

[0091] This invention uses a resist constituent which was described above again, and also offers the approach of forming a resist pattern, especially a positive resist pattern on a processed substrate. Formation of the positive resist pattern of this invention can usually be carried out as follows. First, on a processed substrate, the resist constituent of this invention is applied and the resist film is formed. A processed substrate can be a substrate usually used in a semiconductor device and other equipments, and can raise a silicon substrate, a glass substrate, a nonmagnetic ceramic substrate, etc. as some of the examples. Moreover, if needed, above these substrates, the additional layer, for example, a silicon oxide layer, the metal layer for wiring, the interlayer insulation film, the magnetic film, etc. may exist, and various kinds of wiring, a circuit, etc. are made. In order to raise the adhesion of the resist film to it, hydrophobing processing of these substrates may be carried out further again according to the conventional method. As a suitable hydrophobing processing agent, 1, 1, 1, 3, 3, and 3-hexamethyldisilazane (HMDS) etc. can be raised, for example.

[0092] Spreading of a resist constituent can be applied on a processed substrate by making it into a resist solution, as described above. Although spreading of a resist solution has the technique of daily use, such as spin spreading, roll coating, and DIP spreading, especially its spin spreading is useful. Although, as for resist thickness, the range of about 0.1~200 micrometers is recommended, in KrF exposure, 0.1~1.5 micrometers is recommended. In addition, the thickness of the resist film formed can be widely changed according to factors, such as the purpose for spending of the resist film.

[0093] Before the resist film applied on the substrate exposes it alternatively in the radiation for image formation, it is desirable to prebake over about 60 ~ 120 seconds at the temperature of about 60~160 degrees C. This prebaking can be carried out using a heating means in ordinary use in a resist process. As a suitable heating means, a hot plate, infrared-heating oven, microwave heating oven, etc. can be raised.

[0094] Subsequently, it exposes alternatively in the radiation for image formation with the aligner of daily use of the resist film after prebaking. Suitable aligners are a commercial ultraviolet-rays (far-ultraviolet-rays and deep ultraviolet) aligner, an X-ray aligner, an electron beam machine, an excimer stepper, and others. Exposure conditions can choose suitable conditions each time. Especially, in this invention, as stated also in advance, excimer laser (KrF laser with a wavelength of 248nm and ArF laser with a wavelength of 193nm) can be advantageously used as the exposure light source. When it adds, with this application specification, it is a "radiation". When a word is used, the light from these various light sources, i.e., ultraviolet rays, far ultraviolet rays, deep ultraviolet, an electron ray (EB), an X-ray, a laser beam, etc. shall be meant. As a result of this alternative exposure, a radiation is absorbed, and the dissolution inhibitor compound contained to the exposure field of the resist film decomposes, and solubilizes the exposure field concerned to a basic water solution.

[0095] Subsequently, the elimination reaction of the protective group which made the acid the catalyst is produced by carrying out after [exposure] BEKU (PEB) of the resist film after exposure. BEKU after this exposure can be performed like previous prebaking. For example, about 60~150 degrees C of baking temperature are about 100~150 degrees C preferably. After completing BEKU after exposure, the resist film after exposure is developed in the basic water solution as a developer. The developer of daily use, such as a spin developer, a DIP developer, and a spray developer, can be used for this development. Here, the basic water solutions which can be advantageously used as a developer are the water solution of I of the periodic table represented by the potassium hydroxide etc., and the hydroxide of the metal belonging to II group, and a water solution of the organic base which does not contain metal ions, such as tetraalkylammonium hydroxide. Basic water solutions are water solutions, such as tetramethylammonium hydroxide (TMAH) and hydroxylation tetraethylammonium (TEAH), more preferably. Moreover, this basic water solution may contain additives, such as a surfactant, for improvement in the development effect. As a result of development, the exposure field of the resist film carries out dissolution removal, and only an unexposed field remains on a substrate as a resist pattern.

[0096]

[Example] Subsequently, it is related with composition of an acid sensitivity polymer, preparation of a resist

constituent, and formation of a resist pattern, and this invention is explained with reference to the example of shoes. In addition, please understand that the following example is not that to which it is a mere example and the range of this invention is limited by this.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of the example 1 methacrylic-acid (**)–mevalonic lactone ester was carried out was put, a 30ml desiccation methylene chloride, 6g (46.1 millimol) (**)–mevalonic lactone, and 4.82g (46.1 millimol) methacrylic-acid chloride were added, and it stirred at 0 degree C under desiccation nitrogen-gas-atmosphere mind in it. In the obtained solution, 5.1g (50.4 millimol) triethylamine and 10mg N, and N-dimethylamino pyridine were added, and it stirred at 0 degree C in it for 1 hour. After checking disappearance of a raw material by thin-layer chromatography, the reaction solution was moved to the 300ml separating funnel, and 100ml water washed, and the methylene chloride extracted the aqueous phase 3 times. Organic layers were collected, and saturation brine washed, and it was made to dry on anhydrous sodium sulfate. The organic layer after desiccation was filtered through the filter paper, and the solvent of a filtrate was distilled off under reduced pressure. Brown oily matter was obtained. When the obtained oily matter was refined by the silica gel chromatography, it was transparent and colorless and oil-like methacrylic-acid (**)–mevalonic lactone ester was obtained. Yield = 5.94g (65%).

[0097] The result of analysis of the obtained product is as follows. In addition, s in a parenthesis is [a doublet and m of a singlet and d] multiplets.

¹H NMR(CDCL₃, delta, and J in Hz):6. — 05, 5.58 (respectively 1 H), 4.44–4.35 (2H, m), 3.19 (1H, d, J= 17.5), 2.62 (1H, m), 2.60 (1H, d, J= 17.5) and 2.03 (1H, m), and 1. — 91 and 1.66 (H respectively 3 s).

[0098] Moreover, the result of analysis of IR is as follows. In addition, in the lowercase letter bundled with the parenthesis, in s, strong (a little more than) and m mean medium (inside), and w means weak (weakness).

IR (KBr, neat, cm⁻¹) : 2980 (w), 1743 (s), 1714 (s), 1271 (m), 1173 (s), 1161 (s), 1074 (m).

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 2 methacrylic-acid (**)–mevalonic lactone ester / the cyclohexyl methacrylate copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 5.94g (30 millimol) example 1, 5.04g (30 millimol) cyclohexyl methacrylate, 20ml dioxane, and 1.48g (9 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing – desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 7.69g (70%).

[0099] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows.

Weight average molecular weight: 11860 (standard polystyrene conversion).

[0100] Degree of dispersion: 1.45.

IR (KRS-5, cm⁻¹) : 2937, 1726, 1259, 1149, 1112.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 3 methacrylic-acid (**)–mevalonic lactone ester / the p-acetoxy styrene copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 5.94g (30 millimol) example 1, 4.87g (30 millimol) p-acetoxy styrene, 20ml dioxane, and 1.48g (9 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing – desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 7.78g (72%).

[0101] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 75% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows.

Weight average molecular weight: 7620 (standard polystyrene conversion).

[0102] Degree of dispersion: 1.41.

IR (KRS-5, cm⁻¹) : 3193, 1751, 1726, 1218, 1201.

The copolymer compounded in the formation aforementioned example 2 of example 4 resist pattern was dissolved in propylene glycol methyl ether acetate, and it *****ed in the solution 17% of the weight. In addition, 8% of the weight of gamma-butyrolactone was also included in this copolymer solution as an auxiliary solvent. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist

solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 40 mJ/cm² With light exposure, 0.3-micrometer Rhine - and - tooth-space (last shipment) pattern were resolvable.

[0103] Subsequently, when the silicon substrate which applied the resist as mentioned above was held in the parallel monotonous mold RIE system and Ar sputter etching was performed under the conditions of Pmicro=200W, pressure =0.02Torr, and argon (Ar) gas =50sccm, it was checked by thickness measurement that dry etching resistance equivalent to Nagase positive resist NPR-820 (Nagase & Co., Ltd. make) which is a novolak resist is shown.

The copolymer compounded in the formation aforementioned example 3 of example 5 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 18% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 35 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

[0104] Subsequently, when Ar sputter etching of the silicon substrate which applied the resist as mentioned above was carried out by the same technique as said example 4, it was checked that dry etching resistance equivalent to Nagase positive resist NPR-820 (above) is shown. The copolymer compounded in the formation aforementioned example 2 of example 6 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 18% of the weight. The diphenyliodonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat with an ArF excimer laser aligner (the NIKON CORP. make, NA=0.55), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 10 mJ/cm² At light exposure, it is 0.2 micrometers. The last shipment pattern was resolvable.

[0105] Subsequently, when Ar sputter etching of the silicon substrate which applied the resist as mentioned above was carried out by the same technique as said example 4, it was checked that dry etching resistance equivalent to Nagase positive resist NPR-820 (above) is shown. In the fully dried 200ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 7 methacrylic-acid (**) - mevalonic lactone ester / the methacrylic-acid norbornyl copolymer was carried out was put The methacrylic-acid (**) - mevalonic lactone ester of preparation in said 10g (50.5 millimol) example 1, 9.90g (50.5 millimol) methacrylic-acid norbornyl, 33.7ml dioxane, and 2.49g (15.2 millimol) azobisisobutyronitril (azobisobutyronitril) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 3l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 14.33g (72%).

[0106] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows. Weight average molecular weight: 13600 (standard polystyrene conversion).

<DP N=0017> [0107] Degree of dispersion: 1.52.

IR (KRS-5, cm⁻¹) : 2960, 1727, 1259, 1148.

In the fully dried 200ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 8 methacrylic-acid (**) - mevalonic lactone ester / the methacrylic-acid adamantyl copolymer was carried out was put The methacrylic-acid (**) - mevalonic lactone ester of preparation in said 10g (50.5 millimol) example 1, 11.13g (50.5 millimol) methacrylic-acid adamantyl, 33.7ml dioxane, and 2.49g (15.2 millimol) azobisisobutyronitril (azobisobutyronitril) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at

the 3l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 15.85g (75%).

[0108] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows. Weight average molecular weight: 14100 (standard polystyrene conversion).

[0109] Degree of dispersion: 1.41.

IR (KRS-5, cm⁻¹) : 2912, 1722, 1259, 1093.

The copolymer compounded in the formation aforementioned example 7 of example 9 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 38 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 8 of example 10 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 30 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 7 of example 11 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 20 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 8 of example 12 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 23 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of the example 13 methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamantyl copolymer was carried out was put The methacrylic-acid (**)-mevalonic lactone ester of preparation in said 4.96g (25 millimol) example 1, 5.87g (25 millimol) methacrylic-acid 2-methyl-2-adamantyl, 16.7ml dioxane, and 1.23g (9 millimol) azobisisobutyronitril (azobisisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. methanol containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The

powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer powder of the target white was obtained. Yield = 7.44g (68.7%).

[0110] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was lactone:adamanthyl =46.5:53.5. By 96% and 193nm, the permeability in the wavelength of 248nm of this copolymer is 64% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows.

[0111] Weight average molecular weight: 13900 (standard polystyrene conversion).

Degree of dispersion: 1.78.

IR (KRS-5, cm⁻¹) : 2914, 1724, 1259, 1147, 1103.

The copolymer compounded in the formation aforementioned example 13 of example 14 resist pattern was dissolved in propylene glycol methyl ether acetate, and it ****ed in the solution 19% of the weight. In addition, 8% of the weight of gamma-butyrolactone was also included in this copolymer solution as an auxiliary solvent. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 8.3 mJ/cm² With light exposure, 0.25-micrometer Rhine - and - tooth-space (last shipment) pattern were resolvable.

[0112] Subsequently, the silicon substrate which applied the resist (MLMA-MAdMA) as mentioned above was held in the parallel monotonous mold RIE system, and it etched over 5 minutes under the conditions of Pmicro=200W, pressure =0.02Torr, and CF₄ gas =100sccm. The test result as shown in the next table was obtained about the etching rate and the rate ratio (as opposed to NPR-820).

[0113] Moreover, the same etching and the same trial were performed using Nagase positive resist NPR-820 (Nagase& Co., Ltd. make) and PMMA (polymethylmethacrylate) which are a commercial novolak resist for the comparison.

A sample offering resist Etching rate (a part for A/) Rate ratio NPR-820 523 1.00 PMMA 790 1.51 MLMA-MAdMA 610 1.17 From the result shown in the above-mentioned table, the etching resistance of the resist (MLMA-MAdMA) by this invention Nagase who is a novolak resist -- positive -- it is equivalent to it of resist NPR-820, and it being markedly alike and excelling PMMA (polymethylmethacrylate) was checked.

The copolymer compounded in the formation aforementioned example 13 of example 15 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 18% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 7.4 mJ/cm² At light exposure, it is 0.25 micrometers. The last shipment pattern was resolvable.

[0114] subsequently, the place which etched the silicon substrate which applied the resist as mentioned above by the same technique as said example 14 -- Nagase -- positive -- it is equivalent to resist NPR-820 (above), and it was checked that the etching resistance which was markedly alike and was superior to PMMA is shown.

The copolymer compounded in the formation aforementioned example 13 of example 16 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 18% of the weight. The diphenyliodonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat with an ArF excimer laser aligner (the NIKON CORP. make, NA=0.55), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 6 mJ/cm² At light exposure, it is 0.2 micrometers. The last shipment pattern was resolvable.

[0115] subsequently, the place which etched the silicon substrate which applied the resist as mentioned above by the same technique as said example 14 -- Nagase -- positive -- it is equivalent to resist NPR-820 (above), and it was checked that the etching resistance which was markedly alike and was superior to PMMA is shown.

[0116].

[Effect of the Invention] If the resist constituent by this invention is used, a detailed positive resist pattern without swelling can be formed by usable sensibility. moreover, while making the acid sensitivity polymer of this resist constituent into the form of a copolymer, the monomer frame of that 1st monomeric unit is chosen, and there are more than one as a partner of that copolymerization -- it is -- the new high sensitivity resist which can respond also to the exposure light source of ultrashort wavelength like ArF excimer laser can be offered by using a monomeric unit which contains the alicyclic hydrocarbon radical of many rings.

[0117] In the acid sensitivity polymer of the form of a copolymer, it adds to including the 1st protective group (ester group) content carboxyl group in the side chain of the 1st monomeric unit further again. Since both 1st and 2nd ester groups which have protected the carboxyl group can **** by the acid catalyzed reaction when the 2nd protective group (ester group) content carboxyl group is included also in the 2nd monomeric unit at the side chain, The sensibility higher than the case and the high definition of the conventional resist constituent can be acquired easily. Since the chromophore which has an absorbancy index high RIE resistance and big to that copolymer itself since it has the adamantyl radical whose 2nd monomeric unit of that copolymer is the alicyclic hydrocarbon radical of many rings is not included in deep ultra-violet range, this copolymer can also offer the new high sensitivity resist which can respond also to the exposure light source of ultrashort wavelength like ArF excimer laser.

[Translation done.]

* NOTICES *

JPO and NCIP are not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.
2. **** shows the word which can not be translated.
3. In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] When this invention is described in more detail about a resist constituent, it relates to a resist constituent like excimer laser which can use the light of short wavelength as a radiation for image formation more, and can develop negatives with a basic water solution after exposure. This invention relates to the formation approach of the positive type resist pattern which used such a resist constituent again. The resist constituent of this invention belongs under the category of the so-called "chemistry magnification mold resist", is usable sensibility and can form a detailed positive pattern without swelling.

[0002]

[Description of the Prior Art] In recent years, high integration progresses, as for the semiconductor integrated circuit, LSI and VLSI are put in practical use, and the minimum line width of a circuit pattern has reached the field of a subhalf micron. For this reason, it is indispensable to establish ultra-fine processing technology, in the lithography field, as a solution of that demand, the wavelength of the ultraviolet rays of the exposure light source is made to shift to the short wavelength of a far-ultraviolet field, and development of the aligner using the light source of the wavelength of deep ultra-violet range also prospers further. In connection with this, a resist ingredient also has more little absorption of light in the above short wavelength, and development of the ingredient which doubles and has dry etching resistance with sensibility high good serves as pressing need.

[0003] Development of the resist which the photolithography using krypton fluoride excimer laser (it omits the wavelength of 248nm and Following KrF) as a new exposure technique in current and semi-conductor manufacture is studied briskly, and gave good sensibility and definition in such a short wavelength field, and has stability is becoming pressing need. As a resist with the high sensitivity and high resolution which can respond to such a source of short wave Nagamitsu The resist constituent using the concept called a chemistry magnification mold is already presented by H.Ito and others of U.S. IBM. for example, J.M.J.Frechet et al. and Proc.Microcircuit Eng. -- 260 (1982), H.Ito et al., Digest of Technical Papers of 1982 Symposium on VLSI Technology, 86 (1983), H.Ito et al., "Polymers in Electronics", ACS Symposium Series Please refer to the volume 242 and on T.Davidson, ACS, 11 (1984), and U.S. Pat. No. 4,491,628. The fundamental concept of the above-mentioned resist constituent makes catalytic reaction cause in the resist film, raises an apparent quantum yield, and, therefore, is based on attaining high sensitivity-ization of the resist constituent so that I may be easily understood from the above-mentioned reference etc.

[0004] If the chemistry magnification mold resist which be widely study by the current emergency and which added the photo-oxide generating agent (PAG) which have the operation which generate an acid by light to the t-butoxy KARUBONIRUPORI vinyl phenol (t-BOCPVP) be take for an example, in the exposure section of a resist, by heating after exposure, and the so-called "the PEB (postexposure baking)", a t-BOC radical will **** and it will become isobutene and a carbon dioxide. Moreover, the proton acid produced at the time of desorption of t-BOC serves as a catalyst, the above-mentioned deprotection reaction advances continuously, and the polarity of the exposure section changes a lot. In the resist of this example, a resist pattern can be easily formed by choosing the suitable developer which can respond to a big change of the polarity of the exposure section.

[0005] However, since the chemical structure of the resin has constraint, the conventional chemistry magnification mold resist has the problem that it is difficult to satisfy all requirements, such as sensibility, transparency in exposure wavelength, preservation stability, the ease of acquisition, and definition. Especially an important point is constraint of the protective group from which it should be desorbed by heat-treatment under existence of the photo-oxide generating agent in a chemistry magnification mold resist. namely, when the chemistry magnification intervention component which exists in the side chain of the monomeric unit of a film-forming polymer is carboxylate, as for the suitable protective group for the carboxyl group, t-butyl, 1, and 1-dimethylbenzyl radical, a tetrahydropyranyl group, a 3-oxocyclohexyl radical, an isobornyl radical, etc. are known -- **** -- it does not pass but to offer still more effectively the protective group which can act is desired.

[0006]

[Problem(s) to be Solved by the Invention] The purpose of this invention is to be able to follow, to be able to

solve a trouble of a Prior art which was described above, able to use a basic water solution as a developer, have usable sensibility, and offer the new resist constituent which can form a detailed pattern without swelling.

[0007] The purpose of this invention can respond also to the exposure light source of deep ultra-violet range, such as KrF excimer laser, and is again to offer the new resist constituent excellent also in dry etching resistance. Another purpose of this invention is to enlarge the polarity between the exposure section and the unexposed section, and offer the new resist constituent which can form high sensitivity, and high contrast and the pattern which follows and has high resolution.

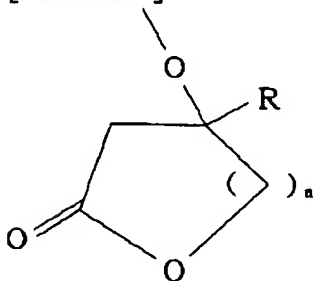
[0008] One purpose is now [of this invention] to offer the approach of forming a resist pattern using such a new resist constituent.

[0009]

[Means for Solving the Problem] That the above-mentioned technical problem should be solved, wholeheartedly, as a result of research, this invention persons acquire the knowledge that it is effective to use what uses the film-forming polymer which has a protective group content carboxyl group for the side chain of a monomeric unit as a polymer used as base material resin in a chemistry magnification mold resist constituent, and has a specific lactone part as a protective group of the carboxyl group of the polymer, and came to complete this invention.

[0010] This invention is a film-forming polymer which has a protective group content carboxyl group in the side chain of a monomeric unit in the one field. The acid sensitivity polymer which can become meltable in a basic water solution when it is insoluble in a the very thing basicity water solution, however the protective group of said carboxyl group is desorbed from a side chain, Lactone part with which said acid sensitivity polymer is expressed by the degree type (I) in that case coming [the photo-oxide generating agent which can generate the acid with which the desorption of the protective group of said carboxyl group can be caused if the radiation for image formation is absorbed and it decomposes] : [0011]

[Formula 4]



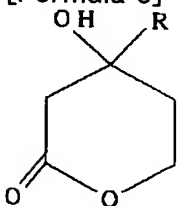
(I)

[0012] It is in the resist constituent in which development is possible in the basic water solution characterized by containing (R may express the alkyl group of the straight chain which has 1-4 carbon atoms, or branched chain, for example, a methyl group, an ethyl group, a propyl group, etc., and these radicals may be a permutation or unsubstituted any, and n is the integer of 1-4 in an upper type) as a protective group of said carboxyl group.

[0013] In the resist constituent by this invention, the acid sensitivity polymer used as the base material resin includes the various polymers from the homopolymer which is used in large semantics, therefore consists only of a single monomeric unit to the copolymer (a 3 component copolymer etc. is included) of such a monomeric unit and the monomeric unit of others of arbitration. at least one of the monomeric units from which the polymer used here constitutes it preferably — and When the polymer takes the form of a copolymer especially, the monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group An acrylate system monomeric unit, i.e., an acrylate system, and a methacrylate system monomeric unit, (Meta) A vinyl phenol system monomeric unit, N-permutation maleimide system monomeric unit, It is what is the monomeric unit which has an ester group containing the alicyclic hydrocarbon part of a styrene system monomeric unit, plurality, or a polycyclic type. Still more preferably an alicyclic hydrocarbon part is the monomeric unit which has the ester group containing the alicyclic hydrocarbon part of the plurality which is an adamantanyl radical and (or) a norbornyl radical, or a polycyclic type.

[0014] Moreover, the lactone part as a protective group of the carboxyl group contained in the side chain in this acid sensitivity polymer is (**)—mevalonic lactone: [0015] preferably expressed by the degree type (IV) although it is said that it can have the structure of arbitration.

[Formula 5]



(IV)

[0016] It is guided from (the inside of a formula and R are the same as said definition). The resist constituent of

this invention gives it to a quartz substrate, and is 1 micrometer of thickness on the substrate further again. When a coat is formed, the permeability in the wavelength (180–300nm) of the exposure light source of deep ultra-violet range is 30% or more preferably. When the above mentioned acid sensitivity polymer takes the gestalt of a copolymer, having the additional protective group content carboxyl group also has the desirable monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group. namely, the monomeric unit containing the 1st protective group content carboxyl group in which an acid sensitivity copolymer contains said lactone part carried out as a protective group -- in addition, you may have the monomeric unit containing the 2nd protective group content carboxyl group, and such a combination is also desirable. Here, the monomeric unit containing the 2nd protective group content carboxyl group is partial: [0017] which has a carboxyl group containing the protective group from which it can be desorbed according to an operation of the additional acid from said photo-oxide generating agent in the side chain of the monomeric unit, and is preferably expressed with it by the degree type (II) in that case.

[Formula 6]



[0018] It is the monomeric unit which contains (R1 expresses the alkyl group of the straight chain which has 1–4 carbon atoms, or branched chain, you may be a permutation or unsubstituted any, and Z expresses two or more atoms required to complete an alicyclic hydrocarbon radical with the carbon atom which R1 combined in an upper type) as a protective group of said carboxyl group.

[0019] Although it is said with various gestalten that the 2nd protective group content carboxyl group may exist, it is preferably expressed by the degree type (III).

[0020]

[Formula 7]



[0021] (In an upper type, R1 and Z are the same as said definition respectively) . The resist constituent of this invention is offered in the form of the solution which dissolved in the solvent preferably chosen from the group which consists of ethyl lactate, methyl amyl ketone, methyl-3-methoxy propionate, ethyl-3-ethoxy propionate, propylene glycol methyl ether acetate, and its mixture. Moreover, this resist solution may contain further the solvent chosen from the group which consists of butyl acetate, gamma-butyrolactone, propylene glycol methyl ether, and its mixture as an auxiliary solvent if needed.

[0022] Moreover, this invention is the approach of forming a resist pattern in the field of another, applies the following resist constituent of process: this invention on a processed substrate, and exposes the formed resist film alternatively with the radiation for image formation which can carry out induction of the decomposition of the photo-oxide generating agent of said resist constituent, and is in the formation approach of the resist pattern characterized by coming to contain developing the resist film after exposure in a basic water solution.

[0023] As for the resist film formed on the processed substrate, in the formation approach of the resist pattern by this invention, it is desirable to present heat-treatment after that, before presenting a selection exposure process with it. That is, by this invention approach, while presenting prebaking processing before the exposure, before developing negatives by being after exposure, postbake processing in which it explained as PEB (postexposure baking) previously is presented with the resist film. These heat-treatment can be advantageously carried out according to a conventional method.

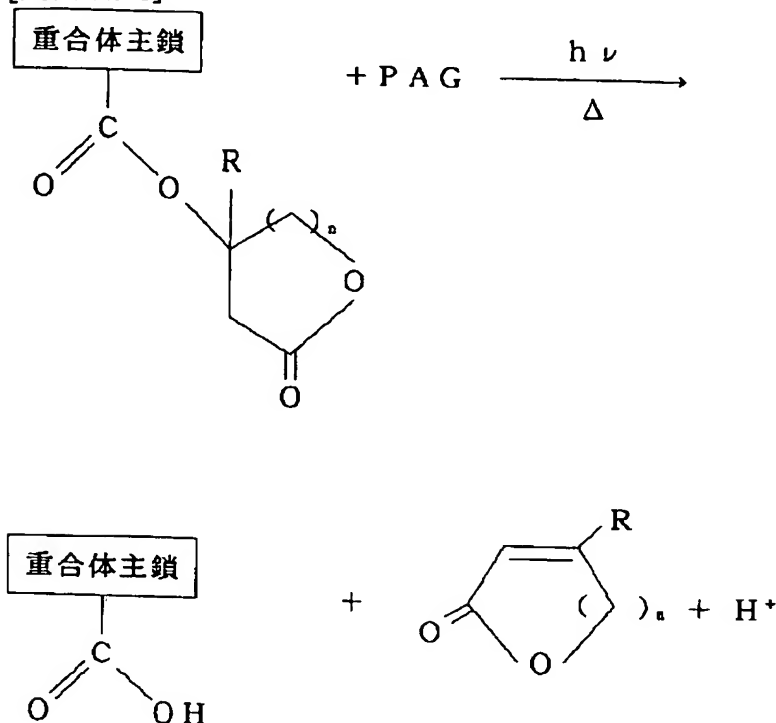
[0024]

[Embodiment of the Invention] The formation approach of the resist constituent by this invention and a resist pattern can be enforced with various desirable gestalten so that he can understand easily from the following detailed explanation. This invention relates to the resist constituent of the chemistry magnification mold in which development is possible with the basic water solution for forming a positive resist pattern on a processed substrate. This resist constituent is a film-forming polymer which has a protective group content carboxyl group in the side chain of the (a) monomeric unit, as described above. The acid sensitivity polymer which can become meltable in a basic water solution when it is insoluble in a the very thing basicity water solution, however the protective group of said carboxyl group is desorbed from a side chain, (b) It comes to contain the photo-oxide generating agent (PAG) which can generate the acid with which the desorption of the protective group of said carboxyl group can be caused if the radiation for image formation is absorbed and it decomposes. Moreover, said acid sensitivity polymer contains the specific lactone part with which it is expressed by the front type (I) as a

protective group of said carboxyl group in that case. If PAG is resist constituent which is as follows when here explains the mechanism of the chemistry magnification in the resist constituent of this invention is exposed to the radiation for image formation after formation of the resist film, it will absorb the radiation and will generate an acid. Subsequently, if the resist film after this exposure is heated, the acid produced previously will act in catalyst and the following reactions will advance in the membranous exposure section.

[0025]

[Formula 8]



[0026] In the resist constituent of this invention, since it set to the acid sensitivity polymer as base material resin and the functional group from which it can be desorbed is easily introduced into the ester part of the monomeric unit with heating under existence of an acid catalyst, by the desorption, proton acid can be reproduced and, therefore, high sensitivity can be attained. Moreover, since a carboxylic acid generates after desorption of a functional group, the exposure section of the resist film becomes meltable to a base, and, therefore, can be developed in a basic water solution. Since the exposure section carries out dissolution removal, the resist pattern obtained is a positive pattern. In addition, in this invention, since pattern formation is performed using a polar change produced in a polymer, a pattern without swelling is obtained.

[0027] Moreover, especially the acid sensitivity polymer used as base material resin in the resist constituent of this invention can be set when it takes the gestalt of a copolymer, and in addition to having easily the functional group from which it can be desorbed with heating under existence of an acid catalyst, also in the 2nd monomeric unit, it can have the same functional group into the ester part of the 1st monomeric unit. In such a case, since the functional group of both in a copolymer may **** by the acid catalyzed reaction, sensibility and definition higher than the copolymer constituted so that the functional group of one of the two's monomeric unit might **** and a soluble change might be given can be reconciled.

[0028] Also although the acid sensitivity polymers used as the base material resin are not conditions which were described above, and the thing limited especially as long as the conditions for the mechanism of chemistry magnification are fulfilled especially in the resist constituent by this invention When acquiring about the same dry etching resistance as a novolak resist is taken into consideration, use of an acrylate system polymer, a methacrylate system polymer, a vinyl phenol system monomeric unit, N-permutation maleimide system polymer, a styrene system polymer, etc. is recommended. When using deep ultraviolet as the exposure light source, the absorption of light of the wavelength of deep ultra-violet range is important for especially an acrylate system and a methacrylate system polymer in a small point. If it puts in another way, when making deep ultraviolet into the exposure light source, it is desirable to use the polymer which has structure which does not contain a chromophore with the aromatic series ring which absorbs the light of deep ultra-violet range greatly and molar extinction coefficients, such as conjugated double bond, large generally.

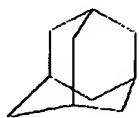
[0029] moreover, in using the exposure light source of an ultrashort wavelength field like argon fluoride (ArF) excimer laser Since the transparency in the wavelength (193nm) of the exposure light source concerned is needed with dry etching resistance, It is the polymer which was described above and the strong aromatic series ring of absorption is not included. Instead Use of the polymer and division acrylate system which have the ester

group which dry etching resistance is high, for example, contains the alicyclic hydrocarbon part of the plurality or polycyclic type represented by an adamantyl radical and the norbornyl radical, and a methacrylate system polymer is recommended. Here, the alicyclic hydrocarbon part which should be contained in an ester group includes well-known various radicals in the field of a chemistry magnification mold resist. If a suitable alicyclic hydrocarbon radical shows the example, it will make the following compounds a frame.

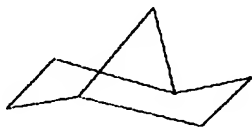
[0030] (1) Adamantane And the derivative (2) norbornane And the derivative (3) par hydronalium anthracene And the derivative (4) par hydronalium naphthalene and derivative (5) tricyclo -- [-- 5.2.1.02, 6] Deccan, its derivative (6) bicyclo hexane, its derivative (7) spiro [4, 4] nonane, derivative (8) spiro [4, 5] Deccan, and its derivative -- the compound of these, respectively : expressed with the following structure expressions [0031]

[Formula 9]

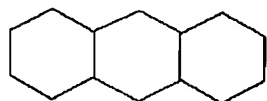
(1)



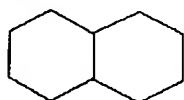
(2)



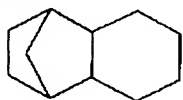
(3)



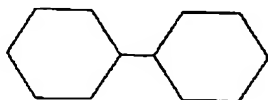
(4)



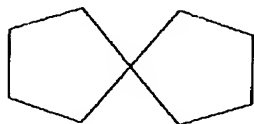
(5)



(6)



(7)



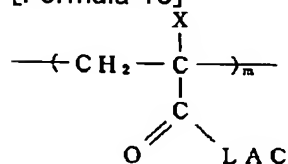
(8)



[0032] Furthermore, the molecular weight (weight average molecular weight and Mw) of an acrylate system polymer (meta) which was described above, and other acid sensitivity polymers can be changed in the large range. Preferably, the range of the molecular weight of this polymer is 2000-1 million, and its range of 3000-50000 is more desirable. Although the acid sensitivity polymer which can be advantageously used in operation of this invention is not necessarily still more specifically limited to what is enumerated below, it includes the following polymers. In addition, m in a formula is the number of monomeric units (repeat unit) required to obtain the above-mentioned weight average molecular weight, and LAC expresses the lactone part of a front type (I), and they are cyano groups, such as low-grade alkyl groups, for example, a methyl group etc., such as the substituent of arbitration, for example, a hydrogen atom, a halogen atom, for example, chlorine, and a bromine, and others except for the case where X has a notice especially.

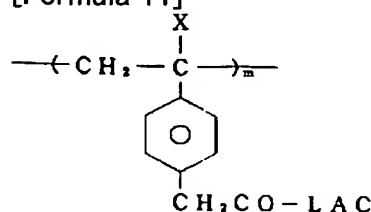
(1) (meta) Acrylate system polymer [0033]

[Formula 10]



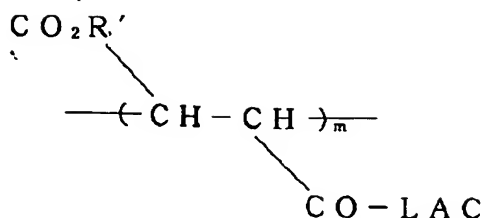
[0034] (2) Vinyl phenol system polymer [0035]

[Formula 11]



[0036] (3) Fumaric-acid system polymer [0037]

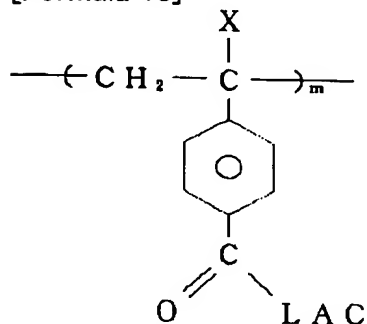
[Formula 12]



[0038] In an upper type, R' expresses said LAC or expresses others for aryloxy groups, for example, a phenoxy group, such as an alkoxy group, for example, a methoxy group, an isopropoxy group, and a t-butoxy radical, a benzyloxy radical, etc.

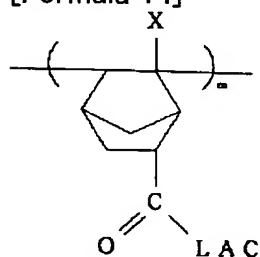
(4) Vinyl benzoic-acid system polymer [0039]

[Formula 13]



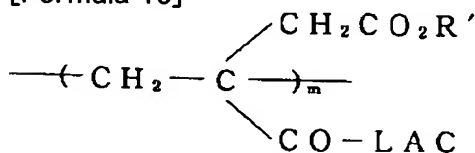
[0040] (5) Norbornene carboxylic-acid system polymer [0041]

[Formula 14]



[0042] (6) Itaconic-acid system polymer [0043]

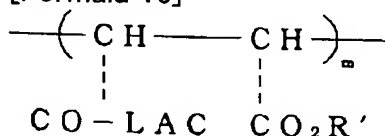
[Formula 15]



[0044] In an upper type, R' is the same as said definition.

(7) Maleic-acid system polymer [0045]

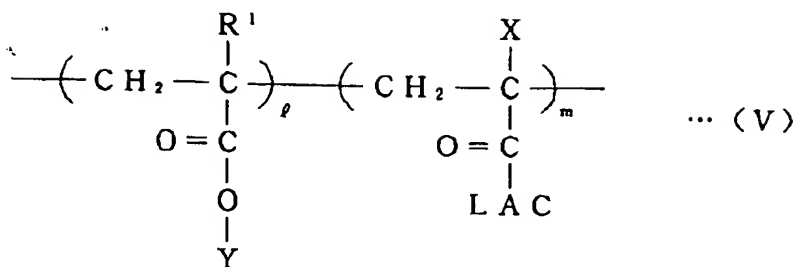
[Formula 16]



[0046] In an upper type, R' is the same as said definition. in addition, also in advance, these polymers were explained -- as -- suitable other monomeric units and ***** -- the copolymers (a 2 component copolymer, 3 component copolymer, etc.) of arbitration may be constituted. The acid sensitivity copolymer which can be used in this invention is as being shown in the following formula (V) and (VI), when the aforementioned (meta) acrylate system polymer is explained with reference to what is made into a subject. In addition, an acrylate (meta) system 3 component copolymer can also be constituted according to this.

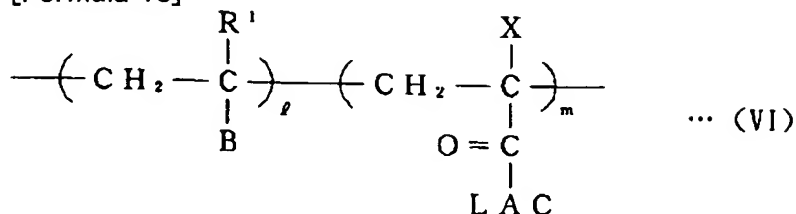
[0047]

[Formula 17]



[0048]

[Formula 18]



[0049] In an upper type, R¹ expresses hydrogen or expresses the substituent of arbitration, for example, a halogen, an alkyl group, a methylol radical, etc. Y Alicyclic radicals, the substituent, for example, the alkyl group, for example, t-butyl etc., of arbitration etc., Adamanthyl, norbornyl, cyclohexyl, tricyclo [5.2.1.0] Deccan, etc. are expressed. For example, B The substituent of arbitration, for example, a carboxyl group etc., is expressed, l and m are the mole ratios of each monomeric unit, and it is l+m=1, and X and LAC are the same as said definition respectively.

[0050] Moreover, if it clarifies in relation to this, the acrylate system polymer with which the usefulness was found out especially in this invention persons and which contains (**)—mevalonic lactone (meta) acrylic ester in a constituent (meta) is new, and is not taught at all by the Prior art. It can reach and other acrylate (meta) system polymers can be prepared using the polymerization method generally used in the chemistry of a polymer also including these things in the gestalt of a copolymer. For example, the acrylate (meta) system polymer of this invention can be advantageously prepared by carrying out the free radical polymerization of the predetermined monomer component in existence of the 2,2'-azobis isobutyronitrile (azobisuisobutironitoriru) as a free radical initiator, although detailed explanation is omitted in this application specification. Moreover, acid sensitivity polymers other than an acrylate (meta) system polymer can be similarly prepared advantageously according to a conventional method.

[0051] By the way, when an acid sensitivity polymer takes the gestalt of a copolymer, the rate of a monomeric unit of having the lactone part of a formula (I) in an ester group before occupying in the copolymer is 20 – 70 % of the weight preferably. If the content of this monomeric unit is less than 20 % of the weight, satisfying patterning will become impossible, and if it exceeds 70 % of the weight reversely [that], it will change to a basic water solution possible [the dissolution]. The content of this monomeric unit is 30 – 60 % of the weight still more preferably.

[0052] Moreover, when the acid sensitivity polymer contained as base material resin in it takes the gestalt of a copolymer in the resist constituent of this invention according to this invention persons' further knowledge, having the additional protective group content carboxyl group, as described above also has the desirable monomeric unit of the polymerization partner of a monomeric unit who has a protective group content carboxyl group. namely, the monomeric unit containing the 1st protective group content carboxyl group in which an acid sensitivity copolymer contains said lactone part carried out as a protective group -- in addition, you may have the monomeric unit containing the 2nd protective group content carboxyl group, and such a combination is desirable. Here, the monomeric unit containing the 2nd protective group content carboxyl group is partial: [0053] which has a carboxyl group containing the protective group from which it can be desorbed according to an operation of the additional acid from said photo-oxide generating agent in the side chain of the monomeric unit, and is preferably expressed with it by the degree type (II) in that case.

[Formula 19]

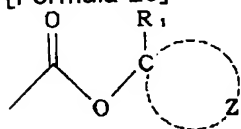


[0054] It is the monomeric unit which contains (R₁ expresses the alkyl group of the straight chain which has 1-4 carbon atoms, or branched chain, you may be a permutation or unsubstituted any, and Z expresses two or more atoms required to complete an alicyclic hydrocarbon radical with the carbon atom which R₁ combined in an upper

type) as a protective group of said carboxyl group. Although it is said with various gestalten that the 2nd protective group content carboxyl group may exist, it is preferably expressed by the degree type (III).

[0055]

[Formula 20]

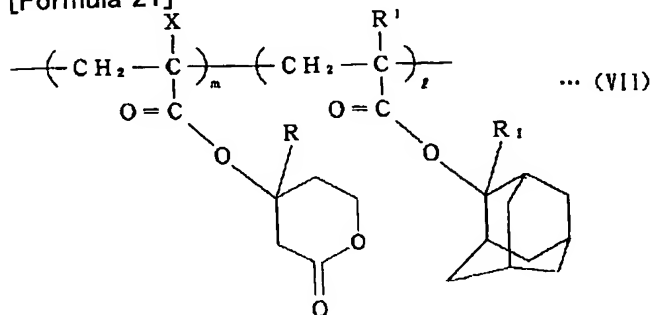


... (III)

[0056] It sets at an upper ceremony and is RI. And Z is the same as said definition respectively. When it states in more detail, the acid sensitivity copolymer which each monomeric unit has the protective group content carboxyl group, and can use advantageously in operation of this invention is a copolymer expressed by the degree type (VII) preferably.

[0057]

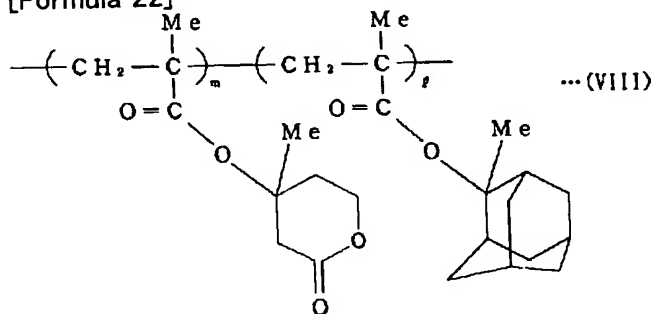
[Formula 21]



[0058] in an upper type, R, RI, and R1, X, m and l are the same as said definition respectively, and the substituents R1 and X combined with the carbon atom of a principal chain are the same — or you may differ and they are a hydrogen atom or a low-grade alkyl group, for example, a methyl group, preferably. The acid sensitivity copolymer which can be used still more advantageously in operation of this invention is a methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamantyl copolymer which follows and is expressed by the degree type (VIII).

[0059]

[Formula 22]



[0060] In an upper type, Me could express the methyl group, this methyl group may be replaced with the hydrogen atom, and m and l are the same as said definition respectively. In such a copolymer and the other same copolymers, since an adamantyl radical is included in the ester section, high dry etching resistance (RIE resistance) can be acquired. If it is going to acquire the RIE resistance of the novolak resist average by which the current general purpose is carried out here, it is required to make into about 50 mol % the content of the methacrylic-acid 2-methyl-2-adamantyl which is the 2nd monomeric unit in a copolymer. Moreover, since this copolymer has the structure which does not contain the strong aromatic series ring of absorption, it is very advantageous about the transparency in ultrashort wavelength (193nm) like argon fluoride (ArF) excimer laser.

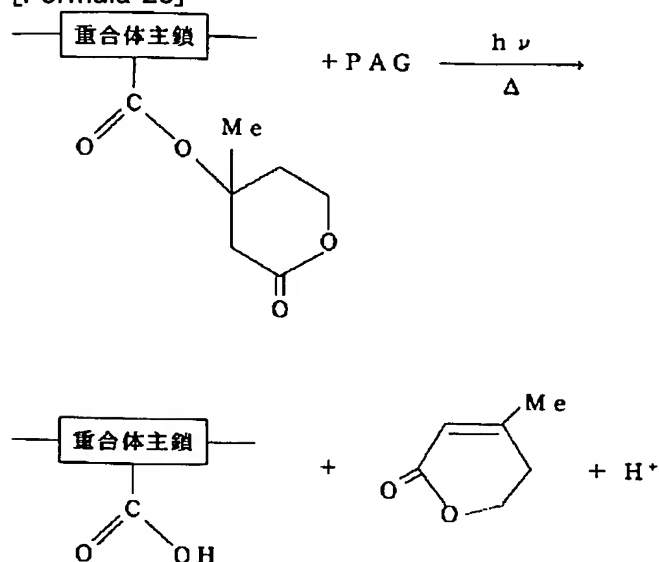
[0061] It is desirable still more desirable that it is generally about 20 - 70 % of the weight, and the content of the methacrylic-acid (**)-mevalonic lactone ester which is the 1st monomeric unit in a copolymer which was described above is about 30 - 60 % of the weight. Moreover, it is desirable still more desirable that it is generally about 20 - 80 % of the weight, and the content of the methacrylic-acid 2-methyl-2-adamantyl which is the 2nd monomeric unit in this copolymer is about 30 - 70 % of the weight. As it already explained that it was little or more abundant than range which each monomeric unit described above, and was contained, un-arranging [of changing to the basic water solution whose satisfying patterning becomes impossible possible / the dissolution] occurs.

[0062] Moreover, a similar reaction [in / the mechanism of the chemistry magnification in a copolymer including the 1st and 2nd monomeric units which were described above is the same as the mechanism of the chemistry magnification in the homopolymer explained previously fundamentally, and / the 2nd monomeric unit] will be added to this. Namely, it is known well that the polymer of an acrylic acid or a methacrylic acid has high transparency by deep ultra-violet range. Moreover, for example, the methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamantyl copolymer expressed by the before type (VIII) Since two kinds of ester sections contained do not contain a chromophore with a big molar extinction coefficient in 190-250nm in the structure, respectively It becomes the high sensitivity resist which will generate an acid if the radiation for image formation of optimum dose is absorbed and it decomposes, and can respond also to the exposure using deep ultraviolet advantageously if the compound (PAG) from which the above-mentioned ester section may be desorbed is combined.

[0063] If PAG is exposed to the radiation for image formation after formation of the resist film, it will absorb the radiation and will generate an acid. Subsequently, if the resist film after this exposure is heated, the acid produced previously will act in catalyst and the following reactions will advance to coincidence separately in the membranous exposure section.

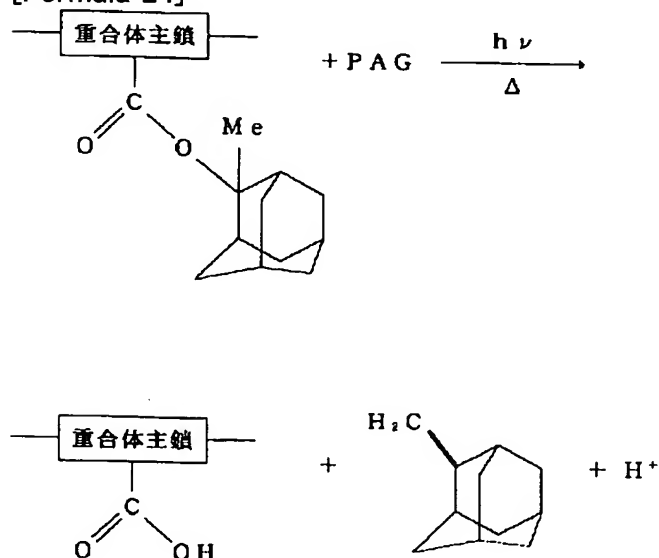
[0064]

[Formula 23]



[0065]

[Formula 24]

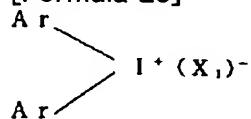


[0066] In a copolymer which was described above, since the functional group from which it can be desorbed is easily introduced into the ester part of the monomeric unit with heating under existence of an acid catalyst, by the desorption, proton acid can be reproduced and, therefore, high sensitivity can be attained. Moreover, since a carboxylic acid generates after desorption of a functional group, the exposure section of the resist film becomes meltable to a base, and, therefore, can be developed in a basic water solution. Since the exposure section carries out dissolution removal, the resist pattern obtained is a positive pattern. In this case, since pattern

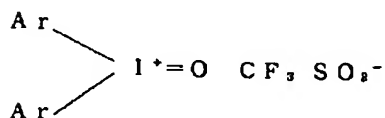
formation is performed using a polar change produced in a polymer, a pattern without swelling is obtained. [0067] Moreover, the photo-oxide generating agent (PAG) used combining an acid sensitivity polymer which was described above in the chemistry magnification mold resist of this invention can be matter which produces proton acid by the exposure of radiations, such as the photo-oxide generating agent generally used in the chemistry of a resist, i.e., ultraviolet rays, far ultraviolet rays, vacuum ultraviolet radiation, an electron ray, an X-ray, and a laser beam. The following is included although a suitable photo-oxide generating agent is not limited to what is enumerated below in operation of this invention.

(1) Iodonium salt expressed by the degree type : [0068]

[Formula 25]



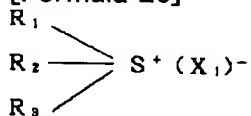
又は



[0069] (In an upper type, Ar expresses alicyclic or radicals, such as a phenyl group permuted by a permutation or an unsubstituted aromatic series radical, for example, a phenyl group, the halogen, the methyl group, t-butyl, an aryl group, etc., and X1 expresses BF₄, BF₆, PF₆, AsF₆, SbF₆, CF₃SO₃, ClO₄, etc.)

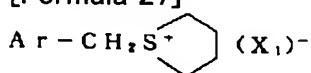
(2) Sulfonium salt expressed by the degree type : [0070]

[Formula 26]



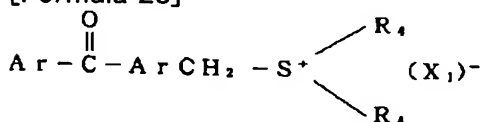
[0071]

[Formula 27]



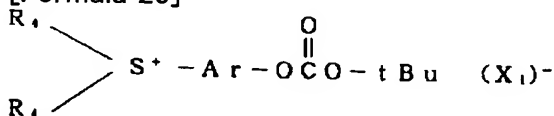
[0072]

[Formula 28]



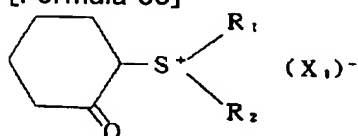
[0073]

[Formula 29]



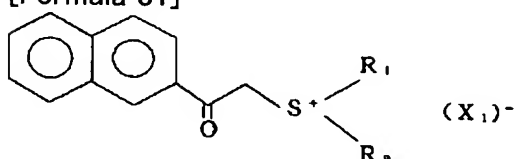
[0074]

[Formula 30]



[0075]

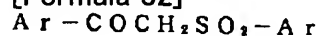
[Formula 31]



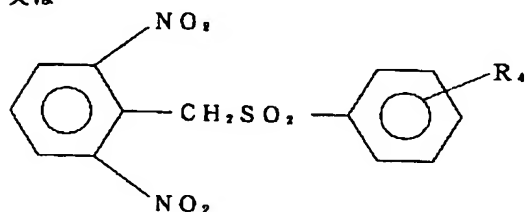
[0076] (In an upper type, R1, R2, R3, and R4 are the same -- or you may differ, and, respectively hydrogen is expressed, the substituent of arbitration, for example, a halogen, an alkyl group, an aryl group, etc. are expressed, R1, R2, and R3 are phenyl groups etc., R4 is a methyl group etc., and Ar and X1 are the same as said definition respectively)

(3) Sulfonate expressed by the degree type : [0077]

[Formula 32]



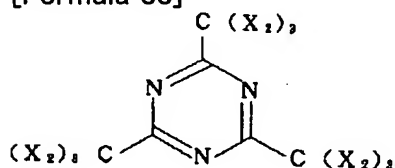
又は



[0078] (In an upper type, Ar and R4 are the same as said definition)

(4) OKISA azole derivative expressed by the degree type : [0079]

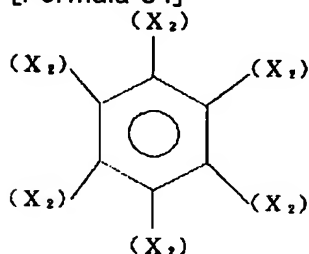
[Formula 33]



[0080] (In an upper type, X2 is a halogen, for example, Cl and Br, or I, however it is -CX3 One of the radicals may be a permutation, an unsubstituted aryl group, or an alkenyl radical)

(5) Halogenide expressed by the degree type : [0081]

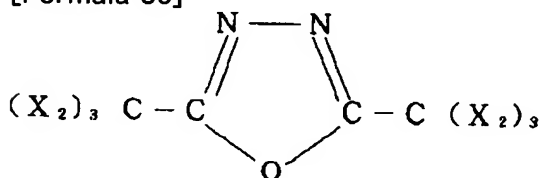
[Formula 34]



[0082] (In an upper type, X2 is the same as said definition)

(6) s-triazine derivative expressed by the degree type : [0083]

[Formula 35]

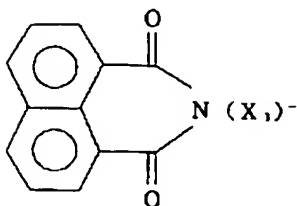
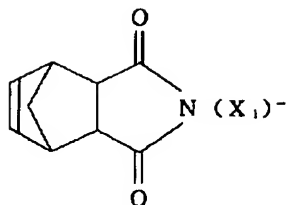
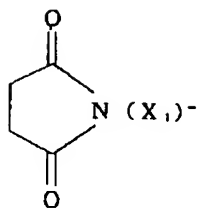


[0084] (In an upper type, X2 is a halogen, for example, Cl and Br, or I, however it is -CX3 One of the radicals may be a permutation, an unsubstituted aryl group, or an alkenyl radical)

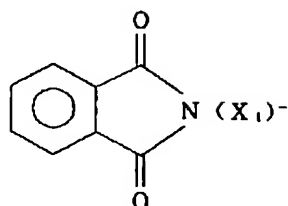
(7) Disulfon derivative: $\text{Ar}-\text{SO}_2-\text{SO}_2-\text{Ar}$ expressed by the degree type (in an upper type, Ar is the same as said definition)

(8) Imide compound expressed by the degree type : [0085]

[Formula 36]



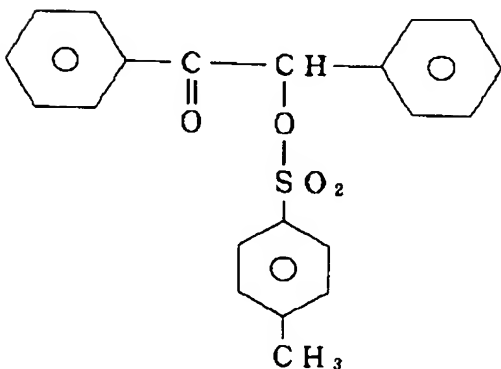
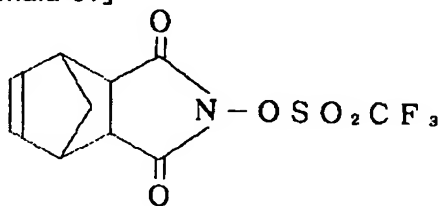
又は



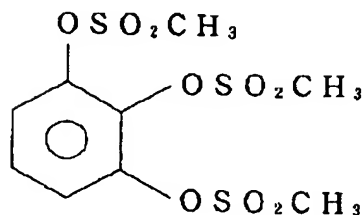
[0086] (In an upper type, X1 is the same as said definition)

(9) In addition, (the sulfonates expressed by the degree type) : [0087]

[Formula 37]



又は



[0088] These photo-oxide generating agents can be used in various amount into the resist constituent of this invention. According to this invention persons' knowledge, the amount of the photo-oxide generating agent used is 0.1 - 50 % of the weight on the basis of the whole quantity of a polymer preferably. When the amount of this photo-oxide generating agent exceeds 50 % of the weight, it becomes impossible to already perform patterning as a result of light being absorbed too much. The amount of the photo-oxide generating agent used is 1 - 15 % of the weight on the basis of the whole quantity of a polymer still more preferably.

[0089] Moreover, it is desirable to take into consideration the structure of a polymer and a photo-oxide generating agent and the amount of the photo-oxide generating agent used so that the transmission (value when forming the resist coat of 1 micrometer of thickness on a quartz substrate) in the exposure wavelength of the resist constituent of this invention which consists of an acid sensitivity polymer and a photo-oxide generating agent may become 30% or more in relation to the above. The resist constituent of this invention can be dissolved in a suitable organic solvent, and the above-mentioned acid sensitivity polymer and the above-

mentioned photo-oxide generating agent can usually be advantageously used for it in the form of a resist solution. An organic solvent useful to preparation of a resist solution is not limited to these, although ethyl lactate, methyl amyl ketone, methyl-3-methoxy propionate, ethyl-3-ethoxy propionate, propylene glycol methyl ether acetate, etc. are recommended. Although these solvents may be used independently, two or more kinds of solvents may be mixed and used for them if needed. Although especially the amount of these solvents used is not limited, it is desirable to use it in sufficient amount to obtain the suitable viscosity for spreading of spin spreading etc. and desired resist thickness.

[0090] In addition to a solvent (it is called especially the main solvent) which was described above, with the resist solution of this invention, an auxiliary solvent may be used if needed. Although use of an auxiliary solvent is unnecessary, when a solute with low solubility is used depending on the solubility of a solute, it is 10 – 20 % of the weight usually preferably [adding in 1 – 30% of the weight of an amount to the main solvent], and more preferably. Although the example of a useful auxiliary solvent is not limited to what also enumerates these below, it includes butyl acetate, gamma-butyrolactone, propylene glycol methyl ether, etc.

[0091] This invention uses a resist constituent which was described above again, and also offers the approach of forming a resist pattern, especially a positive resist pattern on a processed substrate. Formation of the positive resist pattern of this invention can usually be carried out as follows. First, on a processed substrate, the resist constituent of this invention is applied and the resist film is formed. A processed substrate can be a substrate usually used in a semiconductor device and other equipments, and can raise a silicon substrate, a glass substrate, a nonmagnetic ceramic substrate, etc. as some of the examples. Moreover, if needed, above these substrates, the additional layer, for example, a silicon oxide layer, the metal layer for wiring, the interlayer insulation film, the magnetic film, etc. may exist, and various kinds of wiring, a circuit, etc. are made. In order to raise the adhesion of the resist film to it, hydrophobing processing of these substrates may be carried out further again according to the conventional method. As a suitable hydrophobing processing agent, 1, 1, 1, 3, 3, and 3-hexamethyldisilazane (HMDS) etc. can be raised, for example.

[0092] Spreading of a resist constituent can be applied on a processed substrate by making it into a resist solution, as described above. Although spreading of a resist solution has the technique of daily use, such as spin spreading, roll coating, and DIP spreading, especially its spin spreading is useful. Although, as for resist thickness, the range of about 0.1–200 micrometers is recommended, in KrF exposure, 0.1–1.5 micrometers is recommended. In addition, the thickness of the resist film formed can be widely changed according to factors, such as the purpose for spending of the resist film.

[0093] Before the resist film applied on the substrate exposes it alternatively in the radiation for image formation, it is desirable to prebake over about 60 – 120 seconds at the temperature of about 60–160 degrees C. This prebaking can be carried out using a heating means in ordinary use in a resist process. As a suitable heating means, a hot plate, infrared-heating oven, microwave heating oven, etc. can be raised.

[0094] Subsequently, it exposes alternatively in the radiation for image formation with the aligner of daily use of the resist film after prebaking. Suitable aligners are a commercial ultraviolet-rays (far-ultraviolet-rays and deep ultraviolet) aligner, an X-ray aligner, an electron beam machine, an excimer stepper, and others. Exposure conditions can choose suitable conditions each time. Especially, in this invention, as stated also in advance, excimer laser (KrF laser with a wavelength of 248nm and ArF laser with a wavelength of 193nm) can be advantageously used as the exposure light source. When it adds, with this application specification, it is a "radiation". When a word is used, the light from these various light sources, i.e., ultraviolet rays, far ultraviolet rays, deep ultraviolet, an electron ray (EB), an X-ray, a laser beam, etc. shall be meant. As a result of this alternative exposure, a radiation is absorbed, and the dissolution inhibitor compound contained to the exposure field of the resist film decomposes, and solubilizes the exposure field concerned to a basic water solution.

[0095] Subsequently, the elimination reaction of the protective group which made the acid the catalyst is produced by carrying out after [exposure] BEKU (PEB) of the resist film after exposure. BEKU after this exposure can be performed like previous prebaking. For example, about 60–150 degrees C of baking temperature are about 100–150 degrees C preferably. After completing BEKU after exposure, the resist film after exposure is developed in the basic water solution as a developer. The developer of daily use, such as a spin developer, a DIP developer, and a spray developer, can be used for this development. Here, the basic water solutions which can be advantageously used as a developer are the water solution of I of the periodic table represented by the potassium hydroxide etc., and the hydroxide of the metal belonging to II group, and a water solution of the organic base which does not contain metal ions, such as tetraalkylammonium hydroxide. Basic water solutions are water solutions, such as tetramethylammonium hydroxide (TMAH) and hydroxylation tetraethylammonium (TEAH), more preferably. Moreover, this basic water solution may contain additives, such as a surfactant, for improvement in the development effect. As a result of development, the exposure field of the resist film carries out dissolution removal, and only an unexposed field remains on a substrate as a resist pattern.

[0096]

[Example] Subsequently, it is related with composition of an acid sensitivity polymer, preparation of a resist

constituent, and formation of a resist pattern, and this invention is explained with reference to the example of shoes. In addition, please understand that the following example is not that to which it is a mere example and the range of this invention is limited by this.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of the example 1 methacrylic-acid (**)–mevalonic lactone ester was carried out was put, a 30ml desiccation methylene chloride, 6g (46.1 millimol) (**)–mevalonic lactone, and 4.82g (46.1 millimol) methacrylic-acid chloride were added, and it stirred at 0 degree C under desiccation nitrogen-gas-atmosphere mind in it. In the obtained solution, 5.1g (50.4 millimol) triethylamine and 10mg N, and N-dimethylamino pyridine were added, and it stirred at 0 degree C in it for 1 hour. After checking disappearance of a raw material by thin-layer chromatography, the reaction solution was moved to the 300ml separating funnel, and 100ml water washed, and the methylene chloride extracted the aqueous phase 3 times. Organic layers were collected, and saturation brine washed, and it was made to dry on anhydrous sodium sulfate. The organic layer after desiccation was filtered through the filter paper, and the solvent of a filtrate was distilled off under reduced pressure. Brown oily matter was obtained. When the obtained oily matter was refined by the silica gel chromatography, it was transparent and colorless and oil-like methacrylic-acid (**)–mevalonic lactone ester was obtained. Yield = 5.94g (65%).

[0097] The result of analysis of the obtained product is as follows. In addition, s in a parenthesis is [a doublet and m of a singlet and d] multiplets.

¹H NMR(CDCL₃, delta, and J in Hz):6. -- 05, 5.58 (respectively 1 H), 4.44–4.35 (2H, m), 3.19 (1H, d, J= 17.5), 2.62 (1H, m), 2.60 (1H, d, J= 17.5) and 2.03 (1H, m), and 1. — 91 and 1.66 (H respectively 3 s).

[0098] Moreover, the result of analysis of IR is as follows. In addition, in the lowercase letter bundled with the parenthesis, in s, strong (a little more than) and m mean medium (inside), and w means weak (weakness).

IR (KBr, neat, cm⁻¹) : 2980 (w), 1743 (s), 1714 (s), 1271 (m), 1173 (s), 1161 (s), 1074 (m).

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 2 methacrylic-acid (**)–mevalonic lactone ester / the cyclohexyl methacrylate copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 5.94g (30 millimol) example 1, 5.04g (30 millimol) cyclohexyl methacrylate, 20ml dioxane, and 1.48g (9 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing – desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 7.69g (70%).

[0099] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows.

Weight average molecular weight: 11860 (standard polystyrene conversion).

[0100] Degree of dispersion: 1.45.

IR (KRS-5, cm⁻¹) : 2937, 1726, 1259, 1149, 1112.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 3 methacrylic-acid (**)–mevalonic lactone ester / the p-acetoxy styrene copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 5.94g (30 millimol) example 1, 4.87g (30 millimol) p-acetoxy styrene, 20ml dioxane, and 1.48g (9 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing – desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 7.78g (72%).

[0101] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 75% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows.

Weight average molecular weight: 7620 (standard polystyrene conversion).

[0102] Degree of dispersion: 1.41.

IR (KRS-5, cm⁻¹) : 3193, 1751, 1726, 1218, 1201.

The copolymer compounded in the formation aforementioned example 2 of example 4 resist pattern was dissolved in propylene glycol methyl ether acetate, and it ***** in the solution 17% of the weight. In addition, 8% of the weight of gamma-butyrolactone was also included in this copolymer solution as an auxiliary solvent. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist

solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 40 mJ/cm² With light exposure, 0.3-micrometer Rhine - and - tooth-space (last shipment) pattern were resolvable.

[0103] Subsequently, when the silicon substrate which applied the resist as mentioned above was held in the parallel monotonous mold RIE system and Ar sputter etching was performed under the conditions of Pmicro=200W, pressure =0.02Torr, and argon (Ar) gas =50sccm, it was checked by thickness measurement that dry etching resistance equivalent to Nagase positive resist NPR-820 (Nagase& Co., Ltd. make) which is a novolak resist is shown.

The copolymer compounded in the formation aforementioned example 3 of example 5 resist pattern was dissolved in ethyl lactate, and it *****ed in the solution 18% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 35 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

[0104] Subsequently, when Ar sputter etching of the silicon substrate which applied the resist as mentioned above was carried out by the same technique as said example 4, it was checked that dry etching resistance equivalent to Nagase positive resist NPR-820 (above) is shown. The copolymer compounded in the formation aforementioned example 2 of example 6 resist pattern was dissolved in ethyl lactate, and it *****ed in the solution 18% of the weight. The diphenyliodonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 110 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat with an ArF excimer laser aligner (the NIKON CORP. make, NA=0.55), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 10 mJ/cm² At light exposure, it is 0.2 micrometers. The last shipment pattern was resolvable.

[0105] Subsequently, when Ar sputter etching of the silicon substrate which applied the resist as mentioned above was carried out by the same technique as said example 4, it was checked that dry etching resistance equivalent to Nagase positive resist NPR-820 (above) is shown. In the fully dried 200ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 7 methacrylic-acid (**)–mevalonic lactone ester / the methacrylic-acid norbornyl copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 10g (50.5 millimol) example 1, 9.90g (50.5 millimol) methacrylic-acid norbornyl, 33.7ml dioxane, and 2.49g (15.2 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 3l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 14.33g (72%).

[0106] 1H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows. Weight average molecular weight: 13600 (standard polystyrene conversion).

<DP N=0017> [0107] Degree of dispersion: 1.52.

IR (KRS-5, cm⁻¹) : 2960, 1727, 1259, 1148.

In the fully dried 200ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of example 8 methacrylic-acid (**)–mevalonic lactone ester / the methacrylic-acid adamantyl copolymer was carried out was put The methacrylic-acid (**)–mevalonic lactone ester of preparation in said 10g (50.5 millimol) example 1, 11.13g (50.5 millimol) methacrylic-acid adamantyl, 33.7ml dioxane, and 2.49g (15.2 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at

the 3l. water-ethanol mixed solution containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer of the target white was obtained. Yield = 15.85g (75%).

[0108] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was 1:1. The permeability in the wavelength of 248nm of this copolymer is 95% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency. Moreover, the result of other analysis is as follows. Weight average molecular weight: 14100 (standard polystyrene conversion).

[0109] Degree of dispersion: 1.41.

IR (KRS-5, cm⁻¹) : 2912, 1722, 1259, 1093.

The copolymer compounded in the formation aforementioned example 7 of example 9 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydro oxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. 38 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 8 of example 10 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydro oxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 30 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 7 of example 11 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydro oxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 20 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

The copolymer compounded in the formation aforementioned example 8 of example 12 resist pattern was dissolved in ethyl lactate, and it ****ed in the solution 17% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydro oxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 23 mJ/cm² At light exposure, it is 0.3 micrometers. The last shipment pattern was resolvable.

In the fully dried 100ml eggplant form flask into which the star rubber to which synthetic Teflon TM coating of the example 13 methacrylic-acid (**)-mevalonic lactone ester / methacrylic-acid 2-methyl-2-adamanthyl copolymer was carried out was put The methacrylic-acid (**)-mevalonic lactone ester of preparation in said 4.96g (25 millimol) example 1, 5.87g (25 millimol) methacrylic-acid 2-methyl-2-adamanthyl, 16.7ml dioxane, and 1.23g (9 millimol) azobisisobutyronitril (azobisuisobutironitoriru) were added, and it stirred at 80 degrees C under nitrogen-gas-atmosphere mind for 8 hours. After diluting a reaction solution with a tetrahydrofuran (THF), it was dropped at the 1l. methanol containing a small amount of hydroquinone. Generated precipitate was carried out the ** exception with the glass filter, and it was made to dry at 0.1mmHg and 45 degrees C for 16 hours. The

powder of the obtained white was again dissolved in THF, and the same precipitate as the above-mentioned thing - desiccation were repeated twice. The copolymer powder of the target white was obtained. Yield = 7.44g (68.7%).

[0110] ¹H From NMR, it became clear that the copolymerization ratio of the obtained copolymer was lactone:adamantyl = 46.5:53.5. By 96% and 193nm, the permeability in the wavelength of 248nm of this copolymer is 64% (on 1 micrometer of thickness, and a quartz substrate), and showed that it excelled in transparency.

Moreover, the result of other analysis is as follows.

[0111] Weight average molecular weight: 13900 (standard polystyrene conversion).

Degree of dispersion: 1.78.

IR (KRS-5, cm⁻¹) : 2914, 1724, 1259, 1147, 1103.

The copolymer compounded in the formation aforementioned example 13 of example 14 resist pattern was dissolved in propylene glycol methyl ether acetate, and it dissolved in the solution 19% of the weight. In addition, 8% of the weight of gamma-butyrolactone was also included in this copolymer solution as an auxiliary solvent. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 8.3 mJ/cm² With light exposure, 0.25-micrometer Rhine - and - tooth-space (last shipment) pattern were resolvable.

[0112] Subsequently, the silicon substrate which applied the resist (MLMA-MAdMA) as mentioned above was held in the parallel monotonous mold RIE system, and it etched over 5 minutes under the conditions of Pmicro=200W, pressure =0.02Torr, and CF₄ gas =100sccm. The test result as shown in the next table was obtained about the etching rate and the rate ratio (as opposed to NPR-820).

[0113] Moreover, the same etching and the same trial were performed using Nagase positive resist NPR-820 (Nagase & Co., Ltd. make) and PMMA (polymethylmethacrylate) which are a commercial novolak resist for the comparison.

A sample offering resist Etching rate (a part for A/) Rate ratio NPR-820 523 1.00 PMMA 790 1.51 MLMA-MAdMA 610 1.17 From the result shown in the above-mentioned table, the etching resistance of the resist (MLMA-MAdMA) by this invention Nagase who is a novolak resist -- positive -- it is equivalent to it of resist NPR-820, and it being markedly alike and excelling PMMA (polymethylmethacrylate) was checked.

The copolymer compounded in the formation aforementioned example 13 of example 15 resist pattern was dissolved in ethyl lactate, and it dissolved in the solution 18% of the weight. The triphenylsulfonium trifluoromethane sulfonate of 5% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat by the KrF excimer laser stepper (NA=0.45), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 7.4 mJ/cm² At light exposure, it is 0.25 micrometers. The last shipment pattern was resolvable.

[0114] subsequently, the place which etched the silicon substrate which applied the resist as mentioned above by the same technique as said example 14 -- Nagase -- positive -- it is equivalent to resist NPR-820 (above), and it was checked that the etching resistance which was markedly alike and was superior to PMMA is shown.

The copolymer compounded in the formation aforementioned example 13 of example 16 resist pattern was dissolved in ethyl lactate, and it dissolved in the solution 18% of the weight. The diphenyliodonium trifluoromethane sulfonate of 2% of the weight of an amount was added to the obtained ethyl lactate solution to the copolymer, and it was made to fully dissolve in it. It is 0.2 micrometers about the obtained resist solution. It is 2000rpm on the silicon substrate which gave the adhesion promoter coat after filtering with a Teflon TM membrane filter. The spin coat was carried out and it prebaked for 60 seconds at 120 degrees C. The resist coat of 0.7 micrometers of thickness was obtained. After exposing this resist coat with an ArF excimer laser aligner (the NIKON CORP. make, NA=0.55), negatives were developed in 2.38% of tetramethylammonium hydroxide (TMAH) water solution, and the rinse was carried out for 60 seconds by deionized water. [100 degrees C] [for 60 seconds] 6 mJ/cm² At light exposure, it is 0.2 micrometers. The last shipment pattern was resolvable.

[0115] subsequently, the place which etched the silicon substrate which applied the resist as mentioned above by the same technique as said example 14 -- Nagase -- positive -- it is equivalent to resist NPR-820 (above), and it was checked that the etching resistance which was markedly alike and was superior to PMMA is shown.

[0116]

[Effect of the Invention] If the resist constituent by this invention is used, a detailed positive resist pattern without swelling can be formed by usable sensibility. moreover, while making the acid sensitivity polymer of this resist constituent into the form of a copolymer, the monomer frame of that 1st monomeric unit is chosen, and there are more than one as a partner of that copolymerization -- it is -- the new high sensitivity resist which can respond also to the exposure light source of ultrashort wavelength like ArF excimer laser can be offered by using a monomeric unit which contains the alicyclic hydrocarbon radical of many rings.

[0117] In the acid sensitivity polymer of the form of a copolymer, it adds to including the 1st protective group (ester group) content carboxyl group in the side chain of the 1st monomeric unit further again. Since both 1st and 2nd ester groups which have protected the carboxyl group can **** by the acid catalyzed reaction when the 2nd protective group (ester group) content carboxyl group is included also in the 2nd monomeric unit at the side chain, The sensibility higher than the case and the high definition of the conventional resist constituent can be acquired easily. Since the chromophore which has an absorbancy index high RIE resistance and big to that copolymer itself since it has the adamantyl radical whose 2nd monomeric unit of that copolymer is the alicyclic hydrocarbon radical of many rings is not included in deep ultra-violet range, this copolymer can also offer the new high sensitivity resist which can respond also to the exposure light source of ultrashort wavelength like ArF excimer laser.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-90637

(43) 公開日 平成9年(1997)4月4日

(51) IntCl. ⁸	識別記号	庁内整理番号	F I	技術表示箇所
G 0 3 F 7/039	5 0 1		G 0 3 F 7/039	5 0 1
	7/004	5 0 3	7/004	5 0 3
	7/30		7/30	
H 0 1 L 21/027			H 0 1 L 21/30	5 0 2 R
				5 6 9 F
審査請求 未請求 請求項の数10 O L (全 19 頁)				

(21) 出願番号 特願平7-312722

(22) 出願日 平成7年(1995)11月30日

(31) 優先権主張番号 特願平7-178717

(32) 優先日 平7(1995)7月14日

(33) 優先権主張国 日本 (J P)

(71) 出願人 000005223

富士通株式会社

神奈川県川崎市中原区上小田中4丁目1番
1号

(72) 発明者 野崎 耕司

神奈川県川崎市中原区上小田中1015番地
富士通株式会社内

(72) 発明者 矢野 映

神奈川県川崎市中原区上小田中1015番地
富士通株式会社内

(74) 代理人 弁理士 石田 敬 (外2名)

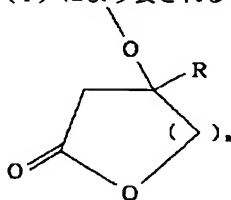
最終頁に続く

(54) 【発明の名称】 レジスト組成物及びレジストパターンの形成方法

(57) 【要約】 (修正有)

【課題】 実用可能な感度で、膨潤のない微細なレジストパターンを形成できるレジスト組成物の提供。

【解決手段】 化学増幅型のレジスト組成物において、光酸発生剤とともにそれに含まれる酸感応性重合体が、次式 (I) により表されるラクトン部分：

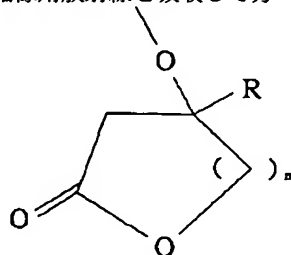


(I)

(上式において、Rは、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基を表し、置換もしくは非置換のいずれであってもよく、そしてnは1～4の整数である)をカルボキシ基の保護基として含んでなるように構成する。

【特許請求の範囲】

【請求項1】 モノマー単位の側鎖に保護基含有カルボキシル基を有する皮膜形成性の重合体であって、自体塩基性水溶液に不溶であり、但し、前記カルボキシル基の保護基が側鎖から脱離した場合、塩基性水溶液に可溶となり得る酸感応性重合体と、結像用放射線を吸収して分



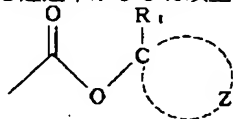
(上式において、Rは、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基を表し、置換もしくは非置換のいずれであってもよく、そしてnは1～4の整数である)を前記カルボキシル基の保護基として含有することを特徴とする、塩基性水溶液で現像可能なレジスト組成物。

【請求項2】 前記ラクトン部分が(±)-メバロニックラクトンから誘導されたものであることを特徴とする、請求項1に記載のレジスト組成物。

【請求項3】 前記酸感応性重合体における重合相手のモノマー単位が、(メタ)アクリレート系モノマー単位、ビニルフェノール系モノマー単位、N-置換マレイミド系モノマー単位、スチレン系モノマー単位及び複数個もしくは多環式の脂環式炭化水素部分を含むエステル基を有するモノマー単位からなる群から選ばれた1員であることを特徴とする、請求項1又は2に記載のレジスト組成物。

【請求項4】 前記モノマー単位の脂環式炭化水素部分が、アダマンチル基及び(又は)ノルボルニル基であることを特徴とする、請求項3に記載のレジスト組成物。

【請求項5】 石英基板上に施してその基板上に膜厚1 μmの皮膜を形成した時、深紫外領域の露光光源の波長(180～300nm)における透過率が30%以上であ



(上式において、R₁及びZは、それぞれ、前記定義に同じである)。

【請求項8】 乳酸エチル、メチルアミルケトン、メチル-3-メトキシプロピオネート、エチル-3-エトキシプロピオネート、プロピレングリコールメチルエーテルアセテート及びその混合物からなる群から選ばれた溶媒に溶解した溶液の形であることを特徴とする、請求項1～7のいずれか1項に記載のレジスト組成物。

【請求項9】 酢酸ブチル、γ-ブチロラクトン、プロ

解すると前記カルボキシル基の保護基の脱離を惹起し得る酸を発生可能である光酸発生剤とを含んでなり、その際、前記酸感応性重合体が、次式(I)により表されるラクトン部分：

【化1】

(I)

ることを特徴とする、請求項1～4のいずれか1項に記載のレジスト組成物。

【請求項6】 前記酸感応性重合体における重合相手のモノマー単位が、そのモノマー単位の側鎖に、追加の、前記光酸発生剤からの酸の作用により脱離可能な保護基を含有するカルボキシル基を有しかつ、その際、次式(II)により表される部分：

【化2】



…(II)

(上式において、R₁は、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基を表し、置換もしくは非置換のいずれであってもよく、そしてZは、R₁が結合した炭素原子とともに脂環式炭化水素基を完成するのに必要な複数個の原子を表す)を前記カルボキシル基の保護基として含有することを特徴とする、請求項1又は2に記載のレジスト組成物。

【請求項7】 前記した追加の保護基含有カルボキシル基が、次式(III)により表されることを特徴とする、請求項6に記載のレジスト組成物。

【化3】

…(III)

ピレングリコールメチルエーテル及びその混合物からなる群から選ばれた溶媒を補助溶媒としてさらに含むことを特徴とする、請求項8に記載のレジスト組成物。

【請求項10】 下記の工程：請求項1～9のいずれか1項に記載のレジスト組成物を被処理基板上に塗布し、形成されたレジスト膜を前記レジスト組成物の光酸発生剤の分解を誘起し得る結像用放射線で選択的に露光し、そして露光後のレジスト膜を塩基性水溶液で現像すること、を含んでなることを特徴とする、レジストパターン

の形成方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、レジスト組成物に関し、さらに詳しく述べると、エキシマレーザのようなより短波長の光を結像用放射線として使用することができ、かつ露光後に塩基性水溶液によって現像を行うことができるレジスト組成物に関する。本発明は、また、このようなレジスト組成物を使用したポジ型レジストパターンの形成方法に関する。本発明のレジスト組成物は、

【0002】

【従来の技術】近年、半導体集積回路は高集積化が進み、LSIやVLSIが実用化されており、配線パターンの最小線幅はサブハーフミクロンの領域に及んでいる。このため、微細加工技術を確立することが必須であり、リソグラフィ分野では、その要求の解決策として、露光光源の紫外線の波長を遠紫外領域の短波長へと移行させており、さらに深紫外領域の波長の光源を用いた露光装置の開発も盛んになってきている。これにともない、レジスト材料も、上記のような短波長での光の吸収がより少なく、感度が良好でかつ高いドライエッチング耐性を合わせもつ材料の開発が急務となっている。

【0003】現在、半導体製造における新しい露光技術として、フッ化クリプトンエキシマレーザ（波長248nm、以下KrFと略す）を用いたフォトリソグラフィが盛んに研究されており、このような短波長領域で良好な感度及び解像性を与え、かつ安定性を兼ね備えたレジストの開発が急務になってきている。このような短波長光源に対応できる高感度かつ高解像度を持ったレジストとして、化学増幅型と呼ばれる概念を用いたレジスト組成物が、米国IBM社のH. Itoらによってすでに提示されている（例えば、J. M. J. Frechetら、Proc. Microcircuit Eng.、260（1982）、H. Itoら、Digest of Technical Papers of 1982 Symposium on VLSI Technology、86（1983）、H. Itoら、"Polymers in Electronics"、ACS Symposium Series 242、T. Davidson編、ACS、11（1984）、そして米国特許第4,491,628号を参照されたい）。上記レジスト組成物の基本概念は、上記の文献等から容易に理解されるように、レジスト膜中で触媒反応を起こさせて見かけの量子収率を向上させ、よって、そのレジスト組成物の高感度化を図ることに基づいている。

【0004】現在非常に広く研究されている、t-ブトキシカルボニルポリビニルフェノール（t-BOCPV

P）に、光によって酸を発生する作用を有する光酸発生剤（PAG）を加えた化学増幅型レジストを例にとってみると、レジストの露光部では、露光後の加熱、いわゆる「PEB（ポストエクスポージャ・ベーキング）」によって、t-BOC基が脱離し、イソブテンと二酸化炭素になる。また、t-BOCの脱離時に生じるプロトン酸が触媒となって、上記の脱保護反応が連鎖的に進行し、露光部の極性が大きく変化する。この例のレジストでは、露光部の極性の大きな変化に対応し得る適切な現像液を選択することにより、容易にレジストパターンを形成することができる。

【0005】しかし、従来の化学増幅型レジストは、その樹脂の化学構造に制約があるために、感度、露光波長における透明性、保存安定性、入手の容易性、そして解像性等の要件をすべて満たすことが難しいという問題をかかえている。特に重要な点は、化学増幅型レジスト中の、光酸発生剤の存在下における加熱処理によって脱離されるべき保護基の制約である。すなわち、皮膜形成性の重合体のモノマー単位の側鎖に存在する化学増幅関与成分がカルボン酸エステルである場合、そのカルボキシル基に適当な保護基は、t-ブチル基、1,1-ジメチルベンジル基、テトラヒドロピラン基、3-オキシシクロヘキシル基、イソボルニル基等が知られているに過ぎず、さらに有効に作用可能な保護基を提供することが望まれている。

【0006】

【発明が解決しようとする課題】本発明の目的は、したがって、上記したような従来の技術の問題点を解決して、現像液として塩基性水溶液を使用することができ、実用可能な感度を有して、膨潤のない微細なパターンを形成することができる新規なレジスト組成物を提供することにある。

【0007】本発明の目的は、また、KrFエキシマレーザ等の深紫外領域の露光光源にも対応可能で、ドライエッチング耐性にもすぐれた新規なレジスト組成物を提供することにある。本発明のもう1つの目的は、露光部と未露光部の間の極性を大きくして、高感度と、高コントラスト及びしたがって高解像度とを有するパターンを形成することができる新規なレジスト組成物を提供することにある。

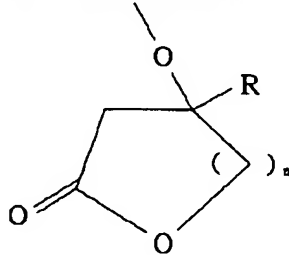
【0008】本発明のいま1つの目的は、このような新規なレジスト組成物を使用してレジストパターンを形成する方法を提供することにある。

【0009】

【課題を解決するための手段】本発明者らは、上記した課題を解決すべく鋭意研究の結果、化学増幅型レジスト組成物において基材樹脂として使用する重合体として、モノマー単位の側鎖に保護基含有カルボキシル基を有する皮膜形成性の重合体を使用し、かつその重合体のカルボキシル基の保護基として、特定のラクトン部分を有す

るものを使用することが有効であるという知見を得、本発明を完成するに至った。

【0010】本発明は、その1つの面において、モノマー単位の側鎖に保護基含有カルボキシル基を有する皮膜形成性の重合体であって、自体塩基性水溶液に不溶であり、但し、前記カルボキシル基の保護基が側鎖から脱離した場合、塩基性水溶液に可溶となり得る酸感性重合



【0012】(上式において、Rは、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基、例えばメチル基、エチル基、プロピル基等を表し、これらの基は置換もしくは非置換のいずれであってもよく、そしてnは1～4の整数である)を前記カルボキシル基の保護基として含有することを特徴とする、塩基性水溶液で現像可能なレジスト組成物にある。

【0013】本発明によるレジスト組成物において、その基材樹脂として用いられる酸感性重合体は、広い意味で用いられており、したがって、単一のモノマー単位のみからなる単独重合体から、そのようなモノマー単位と任意のその他のモノマー単位の共重合体(三成分共重合体等も含む)までの、種々の重合体を包含する。ここで使用する重合体は、好ましくは、それを構成するモノマー単位の少なくとも1つが、そして、特に、その重合体(メタ)アクリレート系モノマー単位、すなわち、アクリレート系及びメタアクリレート系モノマー単位、ビニルフェノール系モノマー単位、N-置換マレイミド系モノマー単位、スチレン系モノマー単位又は複数個もしくは多環式の脂環式炭化水素部分を含むエステル基を有するモノマー単位であるものであり、さらに好ましくは、脂環式炭化水素部分がアダマンチル基及び(又は)ノルボルニル基である複数個もしくは多環式の脂環式炭化水素部分を含むエステル基を有しているモノマー単位であるものである。

【0014】また、かかる酸感性重合体において、その側鎖に含まれるカルボキシル基の保護基としてのラクトン部分は、任意の構造を有することができるというものの、好ましくは、次式(IV)により表される(±)-メバロニックラクトン:

【0015】

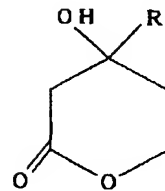
【化5】

体と、結像用放射線を吸収して分解すると前記カルボキシル基の保護基の脱離を惹起し得る酸を発生可能である光酸発生剤とを含んでなり、その際、前記酸感性重合体が、次式(I)により表されるラクトン部分:

【0011】

【化4】

(I)

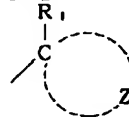


(IV)

【0016】(式中、Rは、前記定義に同じである)から誘導されたものである。さらにまた、本発明のレジスト組成物は、それを石英基板上に施してその基板上に膜厚1μmの皮膜を形成した時、好ましくは、深紫外領域の露光光源の波長(180～300nm)における透過率が30%以上である。前記した酸感性重合体が共重合体の形態をとる場合、保護基含有カルボキシル基を有するモノマー単位の重合相手のモノマー単位が、追加の保護基含有カルボキシル基を有していることも好ましい。すなわち、酸感性共重合体は、前記したラクトン部分を保護基として含有する第1の保護基含有カルボキシル基を含むモノマー単位に加えて、第2の保護基含有カルボキシル基を含むモノマー単位を有していてもよくかつそのような組み合わせも好ましい。ここで、第2の保護基含有カルボキシル基を含むモノマー単位は、好ましくは、そのモノマー単位の側鎖に、追加の、前記光酸発生剤からの酸の作用により脱離可能な保護基を含有するカルボキシル基を有しかつ、その際、次式(II)により表される部分:

【0017】

【化6】

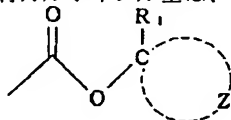


... (II)

【0018】(上式において、R₁は、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基を表し、置換もしくは非置換のいずれであってもよく、そしてZは、R₁が結合した炭素原子とともに脂環式炭化水素基

を完成するのに必要な複数個の原子を表す)を前記カルボキシル基の保護基として含有しているようなモノマー単位である。

【0019】第2の保護基含有カルボキシル基は、いろ



【0021】(上式において、R₁ 及び Z は、それぞれ、前記定義に同じである)。本発明のレジスト組成物は、好ましくは、乳酸エチル、メチルアミルケトン、メチル-3-メトキシプロピオネート、エチル-3-エトキシプロピオネート、プロピレングリコールメチルエーテルアセテート及びその混合物からなる群から選ばれた溶媒に溶解した溶液の形で提供される。また、このレジスト溶液は、必要に応じて、酢酸ブチル、γ-ブチロラクトン、プロピレングリコールメチルエーテル及びその混合物からなる群から選ばれた溶媒を補助溶媒としてさらに含んでいてもよい。

【0022】また、本発明は、そのもう1つの面において、レジストパターンを形成する方法であって、下記の工程：本発明のレジスト組成物を被処理基板上に塗布し、形成されたレジスト膜を前記レジスト組成物の光酸発生剤の分解を誘起し得る結像用放射線で選択的に露光し、そして露光後のレジスト膜を塩基性水溶液で現像すること、を含んでなることを特徴とする、レジストパターンの形成方法にある。

【0023】本発明によるレジストパターンの形成方法において、被処理基板上に形成されたレジスト膜は、それを選択露光工程に供する前とその後、加熱処理に供することが好ましい。すなわち、本発明方法では、レジスト膜を、その露光前にプリベーク処理に供するとともに、露光の後であって現像を行う前、先に PEB (ポストエクスポージャ・ベーク) として説明したところのポストベーク処理に供する。これらの加熱処理は、常

いような形態で存在し得るというものの、好ましくは、次式 (III) により表される。

【0020】

【化7】

… (III)

10 法に従って有利に実施することができる。

【0024】

【発明の実施の形態】本発明によるレジスト組成物及びレジストパターンの形成方法は、以下の詳細な説明から容易に理解できるように、種々の好ましい形態で実施することができる。本発明は、被処理基板上にポジティブのレジストパターンを形成するための、塩基性水溶液により現像可能な化学増幅型のレジスト組成物に関するものである。このレジスト組成物は、前記したように、

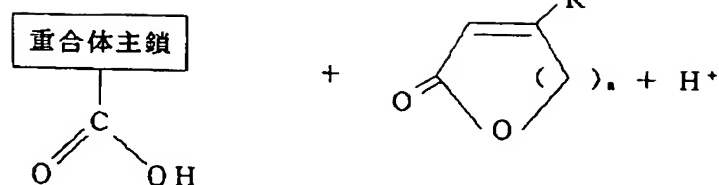
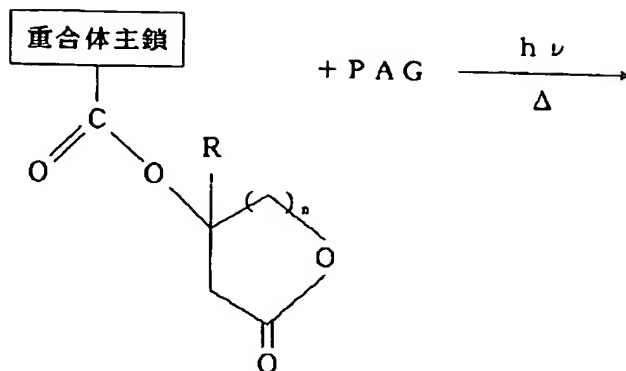
(a) モノマー単位の側鎖に保護基含有カルボキシル基を有する皮膜形成性の重合体であって、自体塩基性水溶液に不溶であり、但し、前記カルボキシル基の保護基が側鎖から脱離した場合、塩基性水溶液に可溶となり得る酸感応性重合体と、(b) 結像用放射線を吸収して分解すると前記カルボキシル基の保護基の脱離を惹起し得る酸を発生可能である光酸発生剤 (PAG) とを含んでなり、また、その際、前記酸感応性重合体は、前式 (I) により表される特定のラクトン部分を前記カルボキシル基の保護基として含有している。ここで、本発明のレジスト組成物における化学増幅のメカニズムを説明すると、次の通りである：レジスト組成物中の PAG は、レジスト膜の形成後に結像用放射線に暴露されると、その放射線を吸収し、酸を発生する。次いで、この露光後のレジスト膜を加熱すると、先に生じた酸が触媒的に作用して、膜の露光部において次のような反応が進行する。

【0025】

【化8】

9

10



20

【0026】本発明のレジスト組成物では、基材樹脂としての酸感応性重合体において、そのモノマー単位のエステル部分に酸触媒の存在下における加熱により容易に脱離可能な官能基を導入しているため、その脱離によってプロトン酸を再生でき、よって、高感度を達成することができる。また、官能基の脱離後にはカルボン酸が生成するため、レジスト膜の露光部は塩基に可溶となり、よって、塩基性水溶液で現像することができる。得られるレジストパターンは、露光部が溶解除去せしめられるので、ポジティブパターンである。なお、本発明では、重合体において生じる極性の変化を利用してパターン形成を行っているため、膨潤のないパターンが得られる。

【0027】また、本発明のレジスト組成物において基材樹脂として用いられる酸感応性重合体は、それが特に共重合体の形態をとる場合において、その第1のモノマー単位のエステル部分に酸触媒の存在下における加熱により容易に脱離可能な官能基を有していることに加えて、第2のモノマー単位においても同様な官能基を有することができる。このような場合には、共重合体中の両方の官能基が酸触媒反応によって脱離し得るので、片方のモノマー単位の官能基が脱離して溶解性の変化を与えるように構成された共重合体よりも一段と高い感度及び解像性を両立させることができる。

【0028】本発明によるレジスト組成物において、その基材樹脂として用いられる酸感応性重合体は、上記したような条件、殊に化学増幅のメカニズムのための条件を満たす限りにおいて特に限定されるものではないけれども、ノボラックレジスト並みのドライエッチング耐性を得ることを考慮に入れた場合、アクリレート系重合体、メタアクリレート系重合体、ビニルフェノール系

モノマー単位、N-置換マレイミド系重合体、スチレン系重合体などの使用が推奨される。特に、アクリレート系及びメタアクリレート系重合体は、露光光源として深紫外線を使用する場合に深紫外領域の波長の光の吸収が小さい点において重要である。換言すると、深紫外線を露光光源とする場合には、一般的に、深紫外領域の光を大きく吸収する芳香族環や、共役二重結合等のモル吸光係数の大きい発色団を含まないような構造を有する重合体を使用することが望ましい。

【0029】また、フッ化アルゴン (ArF) エキシマレーザのような極短波長領域の露光光源を用いる場合には、ドライエッチング耐性とともに対応露光光源の波長 (193nm) における透明性が必要となるため、上記したような重合体であって、吸収の強い芳香族環を含まず、その代わりに、ドライエッチング耐性の高い、例えばアダマンチル基やノルボルニル基に代表される、複数個もしくは多環式の脂環式炭化水素部分を含むエステル基を有する重合体、とりわけアクリレート系及びメタアクリレート系重合体の使用が推奨される。ここで、エステル基に含まれるべき脂環式炭化水素部分は、化学増幅型レジストの分野で公知のいろいろな基を包含する。適当な脂環式炭化水素基は、その一例を示すと、次のような化合物を骨格とするものである。

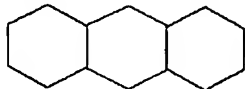
- 【0030】(1) アダマンタン及びその誘導体
 (2) ノルボルナン及びその誘導体
 (3) パーヒドロアントラセン及びその誘導体
 (4) パーヒドロナフタレン及びその誘導体
 (5) トリシクロ [5. 2. 1. 0^{2,6}] デカン及びその誘導体
 (6) ビシクロヘキサン及びその誘導体

50

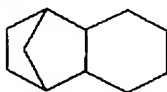
- (7) スピロ〔4, 4〕ノナン及びその誘導体
 (8) スピロ〔4, 5〕デカン及びその誘導体
 これらの化合物は、それぞれ、次のような構造式で表さ
 (1)



(3)



(5)



(7)

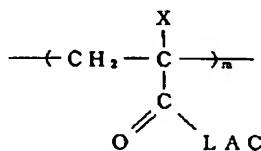


【0032】さらに、上記したような(メタ)アクリレート系重合体及びその他の酸感応性重合体の分子量(重量平均分子量、 M_w)は、広い範囲で変更可能である。好ましくは、かかる重合体の分子量は、2000~1000000の範囲であり、3000~50000の範囲がより好ましい。本発明の実施において有利に使用することのできる酸感応性重合体は、さらに具体的には、以下に列挙するものに限定されるわけではないけれども、次のような重合体を包含する。なお、式中の m は、上記した重量平均分子量を得るのに必要なモノマー単位(繰り返し単位)の数であり、また、LACは、前式(1)のラクトン部分を表し、そして X は、特に断りのある場合を除いて、任意の置換基、例えば、水素原子、ハロゲン原子、例えば塩素、臭素等、低級アルキル基、例えばメチル基等、シアノ基、その他である。

(1) (メタ)アクリレート系重合体

【0033】

【化10】



【0034】(2) ビニルフェノール系重合体

【0035】

【化11】

れる:

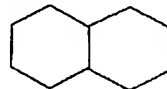
【0031】

【化9】

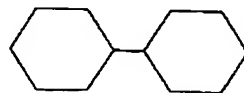
(2)



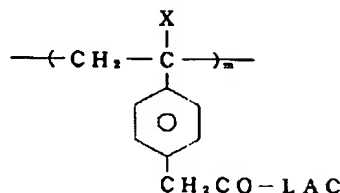
(4)



(6)



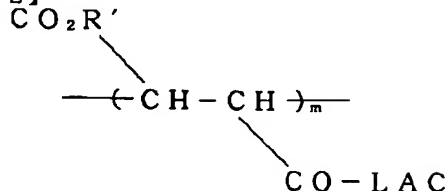
(8)



【0036】(3) フマル酸系重合体

【0037】

【化12】

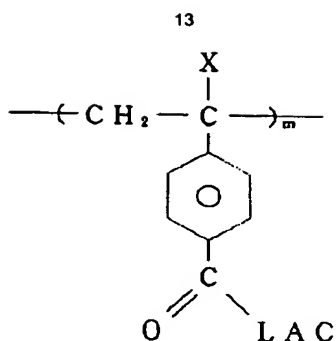


【0038】上式において、 R' は、前記LACを表すかもしくはアルコキシ基、例えばメトキシ基、イソプロポキシ基、 t -ブトキシ基等、アリアルオキシ基、例えばフェノキシ基、ベンジルオキシ基等、その他を表す。

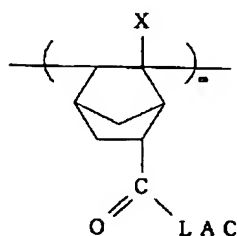
(4) ビニル安息香酸系重合体

【0039】

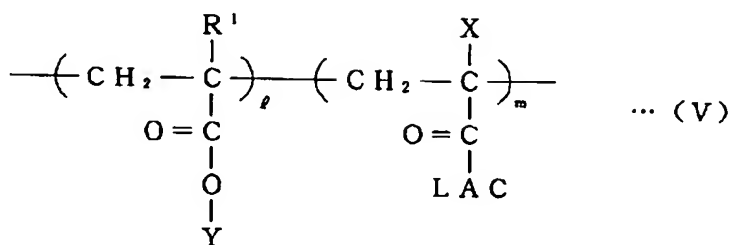
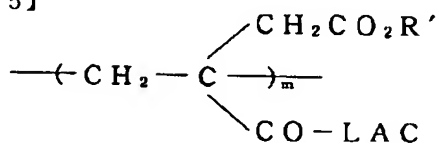
【化13】



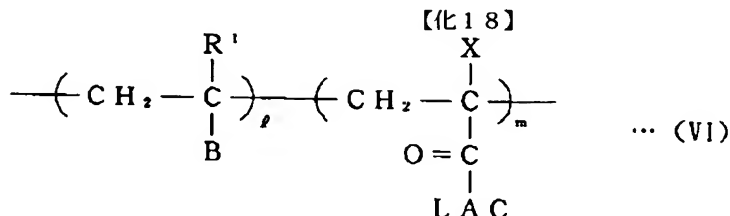
【0040】(5) ノルボルネンカルボン酸系重合体
【0041】
【化14】



【0042】(6) イタコン酸系重合体
【0043】
【化15】



【0048】



【0049】上式において、R'は、水素を表すかもしくは任意の置換基、例えば、ハロゲン、アルキル基、メチロール基などを表し、Yは、任意の置換基、例えば、アルキル基、例えば、t-ブチル基など、脂環式基、例えば、アダマンチル、ノルボルニル、シクロヘキシル、トリシクロ[5.2.1.0]デカンなどを表し、Bは、任意の置換基、例えば、カルボキシ基などを表し、l及び

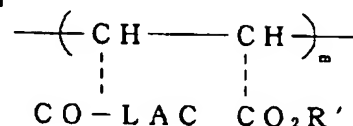
14

【0044】上式において、R'は、前記定義に同じである。

(7) マレイン酸系重合体

【0045】

【化16】



10

【0046】上式において、R'は、前記定義に同じである。なお、これらの重合体は、先にも説明したように、その他の適当なモノマー単位と組合わさって、任意の共重合体（二成分共重合体、三成分共重合体等）を構成していてもよい。本発明において使用することのできる酸感応性共重合体は、前記（メタ）アクリレート系重合体を主体とするものを参照して説明すると、次の式（V）及び（VI）に示す通りである。なお、（メタ）アクリレート系三成分共重合体もこれに準じて構成することができる。

20

【0047】

【化17】

【化18】

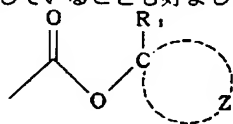
mは、各モノマー単位のモル比であり、l+m=1であり、そしてX及びLACは、それぞれ、前記定義に同じである。

【0050】また、これに関連して明らかにしておくと、本発明者らにおいて特にその有用性が見いだされた、（±）-メバロニックラクトン（メタ）アクリル酸エステルを構成成分に含む（メタ）アクリレート系重合

体は、新規であって、従来の技術ではまったく教示されていない。これらの及びその他の（メタ）アクリレート系重合体は、共重合体の形態にあるものも含めて、ポリマーの化学において一般的に用いられている重合法を使用して調製することができる。例えば、本発明の（メタ）アクリレート系重合体は、本願明細書においては詳細な説明を省略するけれども、所定のモノマー成分をフリーラジカル開始剤としての2, 2'-アゾビスイソブチロニトリル（AIBN）の存在においてフリーラジカル重合させることによって、有利に調製することができる。また、（メタ）アクリレート系重合体以外の酸感応性重合体も、同様に常法に従って有利に調製することができる。

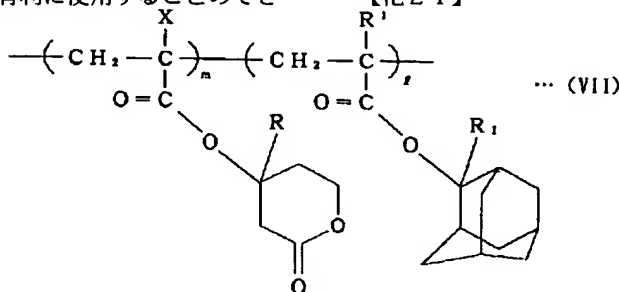
【0051】ところで、酸感応性重合体が共重合体の形態をとる時、その共重合体中に占める前式（I）のラクトン部分をエステル基に有するモノマー単位の割合は、好ましくは、20～70重量%である。このモノマー単位の含有率が20重量%を下回ると、満足のいくパターンニングが不可能となり、また、その反対に70重量%を上回ると、塩基性水溶液に溶解可能に変化してしまう。かかるモノマー単位の含有率は、さらに好ましくは、30～60重量%である。

【0052】また、本発明者らのさらなる知見によると、本発明のレジスト組成物において、その中に基材樹脂として含まれる酸感応性重合体が共重合体の形態をとる時、保護基含有カルボキシル基を有するモノマー単位の重合相手のモノマー単位が、前記したように追加の保護基含有カルボキシル基を有していることも好ましい。



… (III)

【0056】上式において、R₁ 及びZは、それぞれ、前記定義に同じである。さらに詳しく述べると、それぞれのモノマー単位が保護基含有カルボキシル基を有している、本発明の実施において有利に使用することのでき



… (VII)

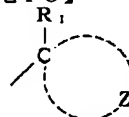
【0058】上式において、R、R₁、R'₁、X、m及びnは、それぞれ、前記定義に同じであり、そして主鎖の炭素原子に結合した置換基R'₁ 及びXは、同一もしくは異なっているとしてもよく、好ましくは、水素原子もしくは低級アルキル基、例えばメチル基である。本発明の実施にお

10

すなわち、酸感応性共重合体は、前記したラクトン部分を保護基として含有する第1の保護基含有カルボキシル基を含むモノマー単位に加えて、第2の保護基含有カルボキシル基を含むモノマー単位を有していてもよくかつそのような組み合わせが好ましい。ここで、第2の保護基含有カルボキシル基を含むモノマー単位は、好ましくは、そのモノマー単位の側鎖に、追加の、前記光酸発生剤からの酸の作用により脱離可能な保護基を含有するカルボキシル基を有しかつ、その際、次式（II）により表される部分：

【0053】

【化19】



… (II)

20

【0054】（上式において、R₁ は、1～4個の炭素原子を有する直鎖もしくは分岐鎖のアルキル基を表し、置換もしくは非置換のいずれであってもよく、そしてZは、R₁ が結合した炭素原子とともに脂環式炭化水素基を完成するのに必要な複数個の原子を表す）を前記カルボキシル基の保護基として含有しているようなモノマー単位である。第2の保護基含有カルボキシル基は、いろいろな形態で存在し得るというものの、好ましくは、次式（III）により表される。

【0055】

【化20】

る酸感応性共重合体は、好ましくは、次式（VII）によって表される共重合体である。

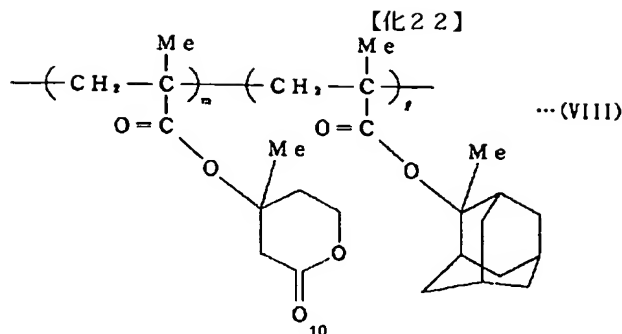
【0057】

【化21】

いてさらに有利に使用することのできる酸感応性共重合体は、したがって、次式（VIII）によって表されるメタクリル酸（±）-メバロニックラクトンエステル/メタクリル酸2-メチルー2-アダマンチル共重合体である。

50

【0059】



【0060】上式において、Meはメチル基を表し、ただし、このメチル基が水素原子に置き替わっていてもよく、そしてm及びnは、それぞれ、前記定義に同じである。このような共重合体及びその他の同様な共重合体では、アダマンチル基をエステル部に含むため、高いドライエッチング耐性（RIE耐性）を得ることができる。ここで、もしも現在汎用されているノボラックレジスト並みのRIE耐性を得ようとするならば、共重合体中の第2のモノマー単位であるメタクリル酸2-メチル-2-アダマンチルの含有量を50モル%程度にすることが必要である。また、この共重合体は吸収の強い芳香族環を含まない構造を有しているので、フッ化アルゴン（ArF）エキシマレーザのような極短波長（193nm）における透明性に関して非常に有利である。

【0061】上記したような共重合体における第1のモノマー単位であるメタクリル酸（±）-メバロニックラクトンエステルの含有量は、一般的に約20～70重量%であるのが好ましく、さらに好ましくは約30～60重量%である。また、かかる共重合体における第2のモノマー単位であるメタクリル酸2-メチル-2-アダマンチルの含有量は、一般的に約20～80重量%であるのが好ましく、さらに好ましくは約30～70重量%である。それぞれのモノマー単位が上記したような範囲よりも少量もしくは多量で含まれると、すでに説明したように、満足のいくパターンニングが不可能となる、塩基性

水溶液に溶解可能に変化してしまう、といった不都合が発生する。

【0062】また、上記したような第1及び第2のモノマー単位を含む共重合体における化学増幅のメカニズムは、基本的には先に説明した単独重合体における化学増幅のメカニズムに同じであり、これに第2のモノマー単位における類似の反応が付加されることになる。すなわち、アクリル酸又はメタクリル酸の重合体は深紫外領域で高い透明性を有することがよく知られており、また、例えば前式（VIII）によって表されるメタクリル酸

（±）-メバロニックラクトンエステル/メタクリル酸2-メチル-2-アダマンチル共重合体は、その構造において、含まれる2種類のエステル部がそれぞれ190～250nmにおいてモル吸光係数の大きな発色団を含まないので、適量の結像用放射線を吸収して分解すると酸を発生し、そして上記のエステル部を脱離させ得る化合物（PAG）を組み合わせれば、深紫外線を用いた露光にも有利に対応できる高感度なレジストとなる。

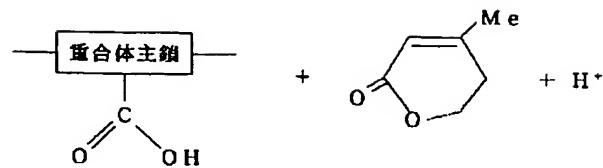
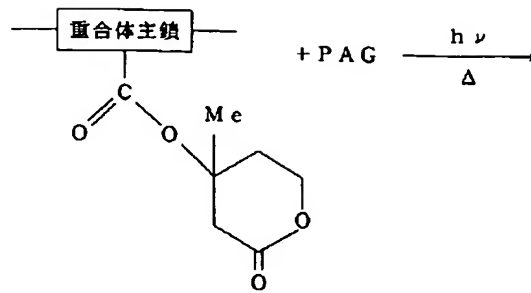
【0063】PAGは、レジスト膜の形成後に結像用放射線に暴露されると、その放射線を吸収し、酸を発生する。次いで、この露光後のレジスト膜を加熱すると、先に生じた酸が触媒的に作用して、膜の露光部において次のような反応が別々にあるいは同時に進行する。

【0064】

【化23】

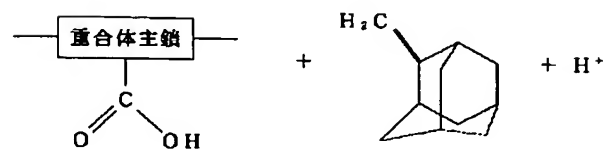
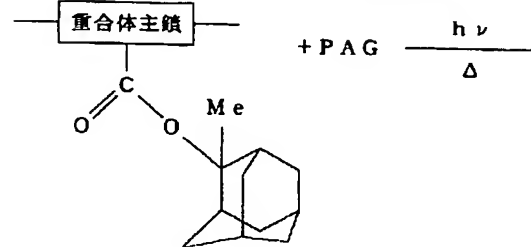
19

20



【0065】

【化24】



【0066】上記したような共重合体では、そのモノマー単位のエステル部分に酸触媒の存在下における加熱により容易に脱離可能な官能基を導入しているの、その脱離によってプロトン酸を再生でき、よって、高感度を達成することができる。また、官能基の脱離後にはカルボン酸が生成するため、レジスト膜の露光部は塩基に可溶となり、よって、塩基性水溶液で現像することができる。得られるレジストパターンは、露光部が溶解除去せしめられるので、ポジティブパターンである。この場合、重合体において生じる極性の変化を利用してパターン形成を行っているの、膨潤のないパターンが得られる。

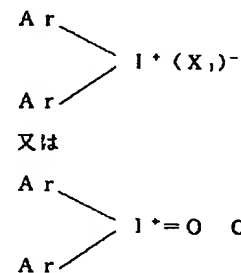
【0067】また、本発明の化学増幅型レジストにおいて上記したような酸感応性重合体と組み合わせて用いられる光酸発生剤（PAG）は、レジストの化学において一般的に用いられている光酸発生剤、すなわち、紫外線、遠紫外線、真空紫外線、電子線、X線、レーザー光な

どの放射線の照射によりプロトン酸を生じる物質であることができる。本発明の実施において適当な光酸発生剤は、以下に列挙するものに限定されないけれども、次のようなものを包含する。

（1）次式により表されるヨードニウム塩：

【0068】

【化25】



【0069】（上式において、Arは、置換もしくは非

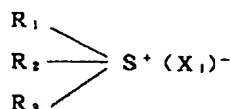
21

置換の芳香族基、例えばフェニル基、ハロゲン、メチル基、*t*-ブチル基、アリール基等で置換されたフェニル基など、又は脂環式基を表し、そして X_1 は、 BF_4 、 BF_6 、 PF_6 、 AsF_6 、 SbF_6 、 CF_3SO_3 、 ClO_4 などを表す)

(2) 次式により表されるスルホニウム塩:

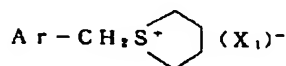
【0070】

【化26】



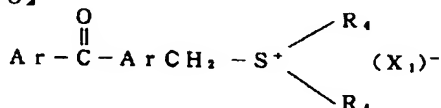
【0071】

【化27】



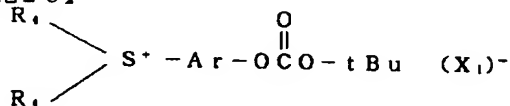
【0072】

【化28】



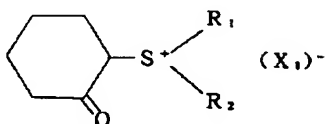
【0073】

【化29】



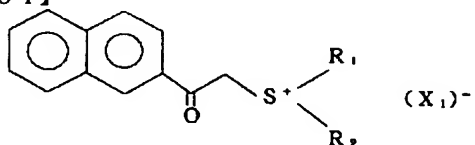
【0074】

【化30】



【0075】

【化31】



【0076】(上式において、 R_1 、 R_2 、 R_3 及び R_4 は、同一もしくは異なっていてもよく、それぞれ、水素を表すかしくは任意の置換基、例えばハロゲン、アルキル基、アリール基などを表し、例えば、 R_1 、 R_2 及び R_3 はフェニル基などであり、そして R_4 はメチル基などであり、そして Ar 及び X_1 は、それぞれ、前記定義に同じである)

22

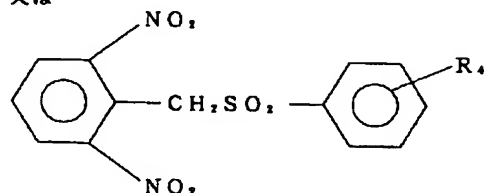
(3) 次式により表されるスルホン酸エステル:

【0077】

【化32】



又は



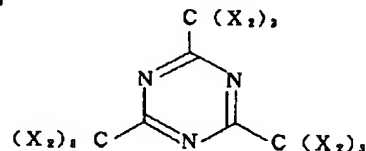
10

【0078】(上式において、 Ar 及び R_4 は、前記定義に同じである)

(4) 次式により表されるオキサアゾール誘導体:

【0079】

【化33】



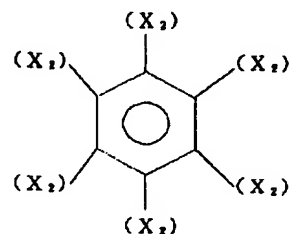
20

【0080】(上式において、 X_2 は、ハロゲン、例えば Cl 、 Br 又は I であり、但し、 $-CX_3$ 基の1つは置換もしくは非置換のアリール基又はアルケニル基であってもよい)

(5) 次式により表されるハロゲン化物:

【0081】

【化34】



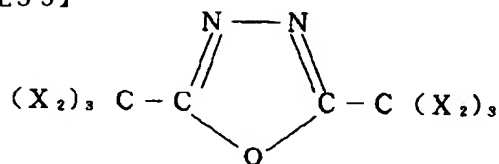
30

【0082】(上式において、 X_2 は前記定義に同じである)

(6) 次式により表されるs-トリアジン誘導体:

【0083】

【化35】



40

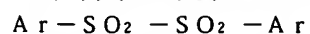
【0084】(上式において、 X_2 は、ハロゲン、例えば Cl 、 Br 又は I であり、但し、 $-CX_3$ 基の1つは置換もしくは非置換のアリール基又はアルケニル基であ

50

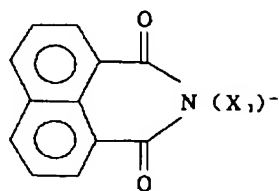
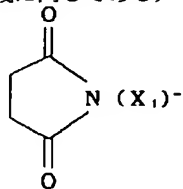
23

てもよい)

(7) 次式により表されるジスルホン誘導体:



(上式において、Arは前記定義に同じである)

【0086】(上式において、X₁は前記定義に同じである)

(9) その他(次式により表されるスルホン酸エステル類):

【0087】

【化37】

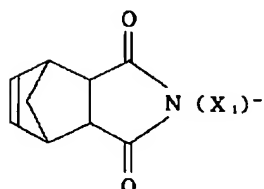
(13)

24

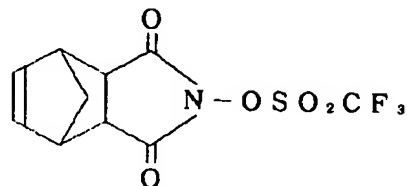
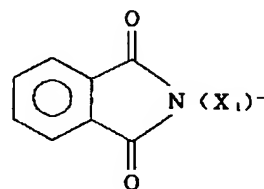
(8) 次式により表されるイミド化合物:

【0085】

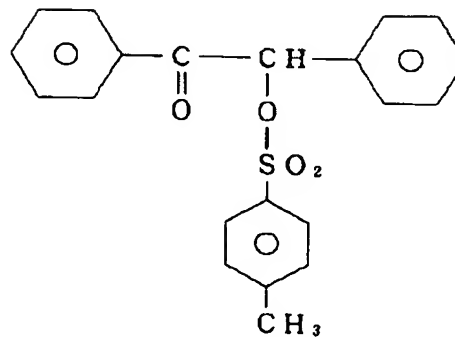
【化36】



又は

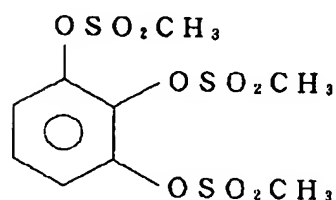


30



又は

40



【0088】これらの光酸発生剤は、本発明のレジスト組成物中においていろいろな量で使用することができる。本発明者らの知見によれば、光酸発生剤の使用量は、好ましくは、重合体の全量を基準にして0.1~50重量%である。この光酸発生剤の量が50重量%を上

回ると、過度に光が吸収されることの結果として、もはやパターンニングを行うことができなくなる。光酸発生剤の使用量は、さらに好ましくは、重合体の全量を基準にして 1~15 重量%である。

【0089】また、上記に関連して、酸感応性重合体と光酸発生剤とからなる本発明のレジスト組成物の露光波長における透過率（膜厚 1 μm のレジスト皮膜を石英基板上に形成した時の値）が 30%以上となるように、重合体及び光酸発生剤の構造ならびに光酸発生剤の使用量を考慮することが望ましい。本発明のレジスト組成物は、通常、上記した酸感応性重合体及び光酸発生剤を適当な有機溶媒に溶解して、レジスト溶液の形で有利に使用することができる。レジスト溶液の調製に有用な有機溶媒は、乳酸エチル、メチルアミルケトン、メチルー 3-メトキシプロピオネート、エチルー 3-エトキシプロピオネート、プロピレングリコールメチルエーテルアセテートなどが推奨されるが、これらに限定されない。これらの溶媒は、単独で使用してもよいが、必要に応じて、2種類以上の溶媒を混合して使用してもよい。これらの溶媒の使用量は、特に限定されないが、スピン塗布等の塗布に適当な粘度及び所望のレジスト膜厚を得るのに十分な量で使用するのが好ましい。

【0090】本発明のレジスト溶液では、必要に応じて、上記したような溶媒（特に主溶媒と呼ぶ）に加えて補助溶媒を使用してもよい。補助溶媒の使用は、溶質の溶解性によっては必要ないが、溶解度の低い溶質を用いた場合、通常、主溶媒に対して 1~30 重量%の量で添加するのが好ましく、より好ましくは 10~20 重量%である。有用な補助溶媒の例は、これも以下に列举するものに限定されないけれども、酢酸ブチル、 γ -ブチロラクトン、プロピレングリコールメチルエーテルなどを包含する。

【0091】本発明はまた、上記したようなレジスト組成物を使用して、被処理基板上にレジストパターン、特にポジティブレジストパターンを形成する方法も提供する。本発明のポジティブレジストパターンの形成は、通常、次のようにして実施することができる。まず、被処理基板上に本発明のレジスト組成物を塗布してレジスト膜を形成する。被処理基板は、半導体装置、その他の装置において通常用いられている基板であることができ、そのいくつかの例として、シリコン基板、ガラス基板、非磁性セラミックス基板などをあげることができる。また、これらの基板の上方には、必要に応じて、追加の層、例えばシリコン酸化物層、配線用金属層、層間絶縁膜、磁性膜などが存在していてもよく、また、各種の配線、回路等が作り込まれていてもよい。さらにまた、これらの基板は、それに対するレジスト膜の密着性を高めるため、常法に従って疎水化処理されていてもよい。適当な疎水化処理剤としては、例えば、1, 1, 1, 3, 3, 3-ヘキサメチルジシラザン（HMDS）などをあ

げることができる。

【0092】レジスト組成物の塗布は、上記したように、それをレジスト溶液として被処理基板上に塗布することができる。レジスト溶液の塗布は、スピン塗布、ロール塗布、ディップ塗布などの常用の技法があるが、特にスピン塗布が有用である。レジスト膜厚は、約 0.1~200 μm の範囲が推奨されるが、KrF 露光の場合は、0.1~1.5 μm が推奨される。なお、形成されるレジスト膜の膜厚は、そのレジスト膜の用途などのファクタに応じて広く変更することができる。

【0093】基板上に塗布したレジスト膜は、それを結像用放射線に選択的に露光する前に、約 60~160℃ の温度で約 60~120 秒間にわたってプリベークすることが好ましい。このプリベークは、レジストプロセスで常用の加熱手段を用いて実施することができる。適当な加熱手段として、例えば、ホットプレート、赤外線加熱オープン、マイクロ波加熱オープンなどをあげることができる。

【0094】次いで、プリベーク後のレジスト膜を常用の露光装置で結像用の放射線に選択的に露光する。適当な露光装置は、市販の紫外線（遠紫外線・深紫外線）露光装置、X線露光装置、電子ビーム露光装置、エキシマステッパ、その他である。露光条件は、その都度、適当な条件を選択することができる。特に、本発明では、先にも述べたように、エキシマレーザ（波長 248nm の KrF レーザ及び波長 193nm の ArF レーザ）を露光光源として有利に使用することができる。付言すると、本願明細書では、“放射線”なる語を用いた場合、これらのいろいろな光源からの光、すなわち、紫外線、遠紫外線、深紫外線、電子線（EB）、X線、レーザ光等を意味するものとする。この選択的露光の結果として、レジスト膜の露光領域に含まれる溶解禁止化合物が放射線を吸収し、分解し、当該露光領域を塩基性水溶液に対して可溶化する。

【0095】次いで、露光後のレジスト膜を露光後ベーク（PEB）することによって、酸を触媒とした保護基の脱離反応を生じさせる。この露光後ベークは、先のプリベークと同様にして行うことができる。例えば、ベーク温度は約 60~150℃、好ましくは約 100~150℃である。露光後ベークを完了した後、露光後のレジスト膜を現像液としての塩基性水溶液で現像する。この現像のため、スピンドベロッパ、ディップデベロッパ、スプレーデベロッパ等の常用の現像装置を使用することができる。ここで、現像液として有利に使用することのできる塩基性水溶液は、水酸化カリウム等に代表される周期律表の I, II 族に属する金属の水酸化物の水溶液や、水酸化テトラアルキルアンモニウム等の金属イオンを含有しない有機塩基の水溶液である。塩基性水溶液は、より好ましくは、水酸化テトラメチルアンモニウム（TMAH）、水酸化テトラエチルアンモニウム（TE

AH)等の水溶液である。また、かかる塩基性水溶液は、その現像効果の向上のため、界面活性剤などのような添加物を含有していてもよい。現像の結果として、レジスト膜の露光領域が溶解除去せしめられて、未露光領域のみがレジストパターンとして基板上に残留する。

【0096】

【実施例】次いで、本発明を酸感応性重合体の合成及びレジスト組成物の調製ならびにレジストパターンの形成に関していくつかの実施例を参照して説明する。なお、下記の実施例はほんの一例であって、これによって本発明の範囲が限定されるものではないことを理解されたい。

例1

メタクリル酸(±)ーメバロニックラクトンエステル/

メタクリル酸シクロヘキシル共重合体の合成
テフロン™ コーティングされたスターラバーを入れた十分に乾燥させた100mlのナス形フラスコに、30mlの乾燥塩化メチレン、6g(46.1ミリモル)の(±)ーメバロニックラクトン及び4.82g(46.1ミリモル)のメタクリル酸クロリドを添加し、乾燥窒素雰囲気下で0℃で攪拌した。得られた溶液に、5.1g(50.4ミリモル)のトリエチルアミン及び10mgのN,N-ジメチルアミノピリジンを添加し、0℃で1時間攪拌した。薄層クロマトグラフィで原料の消失を確認した後、反応溶液を300mlの分液漏斗に移し、100mlの水で洗浄し、そして水相を塩化メチレンで3回抽出した。有機層を集めて飽和食塩水で洗浄し、そして無水硫酸ナトリウム上で乾燥させた。乾燥後の有機層を濾紙でろ過し、そしてろ液の溶媒を減圧下に留去した。褐色の油状物が得られた。得られた油状物をシリカゲルクロマトグラフィで精製したところ、無色透明で油状のメタクリル酸(±)ーメバロニックラクトンエステルが得られた。収量=5.94g(65%)。

【0097】得られた生成物の分析の結果は、次の通りである。なお、カッコ内のsは一重項、dは二重項、そしてmは多重項である。

¹H NMR(CDCl₃, δ, J in Hz): 6.05, 5.58(それぞれ1H), 4.44-4.35(2H, m), 3.19(1H, d, J=17.5), 2.62(1H, m), 2.60(1H, d, J=17.5), 2.03(1H, m), 1.91, 1.66(それぞれ3H, s)。

【0098】また、IRの分析の結果は、次の通りである。なお、カッコでくくった英小文字において、sはstrong(強)、mはmedium(中)、そしてwはweak(弱)を意味する。

IR(KBr, neat, cm⁻¹): 2980(w), 1743(s), 1714(s), 1271(m), 1173(s), 1161(s), 1074(m)。

例2

メタクリル酸(±)ーメバロニックラクトンエステル/メタクリル酸シクロヘキシル共重合体の合成

テフロン™ コーティングされたスターラバーを入れた十分に乾燥させた100mlのナス形フラスコに、5.94g(30ミリモル)の前記例1で調製のメタクリル酸(±)ーメバロニックラクトンエステル、5.04g(30ミリモル)のメタクリル酸シクロヘキシル、20mlのジオキサン及び1.48g(9ミリモル)のアゾビスイソブチロニトリル(AIBN)を添加し、窒素雰囲気下で80℃で8時間攪拌した。反応溶液をテトラヒドロフラン(THF)で希釈した後、少量のヒドロキノンを含む1リットルの水-エタノール混合溶液に滴下した。生成した沈殿をガラスフィルターでろ別し、0.1mmHg及び45℃で16時間乾燥させた。得られた白色の粉末を再びTHFに溶解させ、上記したものと同じ沈殿〜乾燥作業を2度繰り返した。目的とする白色の共重合体を得られた。収量=7.69g(70%)。

【0099】¹H NMRから、得られた共重合体の共重合比は1:1であることが判明した。この共重合体の波長248nmにおける透過率は、95%(膜厚1μm、石英基板上)であり、透明性に優れていることを示した。また、その他の分析の結果は、次の通りである。重量平均分子量: 11860(標準ポリスチレン換算)。

【0100】分散度: 1.45。

IR(KRS-5, cm⁻¹): 2937, 1726, 1259, 1149, 1112。

例3

メタクリル酸(±)ーメバロニックラクトンエステル/p-アセトキシスチレン共重合体の合成

テフロン™ コーティングされたスターラバーを入れた十分に乾燥させた100mlのナス形フラスコに、5.94g(30ミリモル)の前記例1で調製のメタクリル酸(±)ーメバロニックラクトンエステル、4.87g(30ミリモル)のp-アセトキシスチレン、20mlのジオキサン及び1.48g(9ミリモル)のアゾビスイソブチロニトリル(AIBN)を添加し、窒素雰囲気下で80℃で8時間攪拌した。反応溶液をテトラヒドロフラン(THF)で希釈した後、少量のヒドロキノンを含む1リットルの水-エタノール混合溶液に滴下した。生成した沈殿をガラスフィルターでろ別し、0.1mmHg及び45℃で16時間乾燥させた。得られた白色の粉末を再びTHFに溶解させ、上記したものと同じ沈殿〜乾燥作業を2度繰り返した。目的とする白色の共重合体を得られた。収量=7.78g(72%)。

【0101】¹H NMRから、得られた共重合体の共重合比は1:1であることが判明した。この共重合体の波長248nmにおける透過率は、75%(膜厚1μm、石英基板上)であり、透明性に優れていることを示した。また、その他の分析の結果は、次の通りである。

重量平均分子量： 7620（標準ポリスチレン換算）。

【0102】分散度： 1.41。

IR (KRS-5, cm^{-1}) : 3193, 1751, 1726, 1218, 1201。

例4

レジストパターンの形成

前記例2において合成した共重合体をプロピレングリコールメチルエーテルアセテートに溶解して17重量%溶液とした。なお、この共重合体溶液には、補助溶媒として、8重量%の γ -ブチロラクトンも含ませた。得られた溶液に、共重合体に対して5重量%の量のトリフェニルスルホニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を0.2 μm のテフロンTM メンブランフィルタで濾過した後、HMDS処理を施したシリコン基板上に2000rpmでスピコートし、110℃で60秒間プリベークした。膜厚0.7 μm のレジスト皮膜が得られた。このレジスト皮膜をKrFエキシマレーザステッパ (NA=0.45) で露光した後、2.38%のテトラメチルアンモニウムハイドロキシド (TMAH) 水溶液で現像し、脱イオン水で60秒間リンスした。40 mJ/cm^2 の露光量で、0.3 μm ライン・アンド・スペース (L/S) パターンが解像できた。

【0103】次いで、上記のようにしてレジストを塗布したシリコン基板を平行平板型RIE装置に收容し、P μ =200W、圧力=0.02Torr、アルゴン (Ar) ガス=50sccmの条件下でArスパッタエッチングを行ったところ、ノボラックレジストである長瀬ポジティブレジストNPR-820（長瀬産業社製）と同等のドライエッチング耐性を示すことが膜厚測定により確認された。

例5

レジストパターンの形成

前記例3において合成した共重合体を乳酸エチルに溶解して18重量%溶液とした。得られた乳酸エチル溶液に、共重合体に対して2重量%の量のトリフェニルスルホニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を0.2 μm のテフロンTM メンブランフィルタで濾過した後、HMDS処理を施したシリコン基板上に2000rpmでスピコートし、110℃で60秒間プリベークした。膜厚0.7 μm のレジスト皮膜が得られた。このレジスト皮膜をKrFエキシマレーザステッパ (NA=0.45) で露光した後、2.38%のテトラメチルアンモニウムハイドロキシド (TMAH) 水溶液で現像し、脱イオン水で60秒間リンスした。35 mJ/cm^2 の露光量で、0.3 μm L/Sパターンが解像できた。

【0104】次いで、上記のようにしてレジストを塗布したシリコン基板を前記例4と同様な手法によってAr

スパッタエッチングしたところ、長瀬ポジティブレジストNPR-820（前出）と同等のドライエッチング耐性を示すことが確認された。

例6

レジストパターンの形成

前記例2において合成した共重合体を乳酸エチルに溶解して18重量%溶液とした。得られた乳酸エチル溶液に、共重合体に対して2重量%の量のジフェニルヨードニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を0.2 μm のテフロンTM メンブランフィルタで濾過した後、HMDS処理を施したシリコン基板上に2000rpmでスピコートし、110℃で60秒間プリベークした。膜厚0.7 μm のレジスト皮膜が得られた。このレジスト皮膜をArFエキシマレーザ露光装置（ニコン社製、NA=0.55）で露光した後、2.38%のテトラメチルアンモニウムハイドロキシド (TMAH) 水溶液で現像し、脱イオン水で60秒間リンスした。10 mJ/cm^2 の露光量で、0.2 μm L/Sパターンが解像できた。

【0105】次いで、上記のようにしてレジストを塗布したシリコン基板を前記例4と同様な手法によってArスパッタエッチングしたところ、長瀬ポジティブレジストNPR-820（前出）と同等のドライエッチング耐性を示すことが確認された。

例7

メタクリル酸（±）-メバロニックラクトンエステル／メタクリル酸ノルボルニル共重合体の合成

テフロンTM コーティングされたスターラバーを入れた十分に乾燥させた200mlのナス形フラスコに、10g（50.5ミリモル）の前記例1で調製のメタクリル酸（±）-メバロニックラクトンエステル、9.90g（50.5ミリモル）のメタクリル酸ノルボルニル、33.7mlのジオキサン及び2.49g（15.2ミリモル）のアゾビスイソブチロニトリル (AIBN) を添加し、窒素雰囲気下に80℃で8時間攪拌した。反応溶液をテトラヒドロフラン (THF) で希釈した後、少量のヒドロキノンを含む3リットルの水-エタノール混合溶液に滴下した。生成した沈殿をガラスフィルターでろ別し、0.1mmHg及び45℃で16時間乾燥させた。得られた白色の粉末を再びTHFに溶解させ、上記したものと同じ沈殿～乾燥作業を2度繰り返した。目的とする白色の共重合体が得られた。収量=14.33g（72%）。

【0106】¹H NMRから、得られた共重合体の共重合比は1:1であることが判明した。この共重合体の波長248nmにおける透過率は、95%（膜厚1 μm 、石英基板上）であり、透明性に優れていることを示した。また、その他の分析の結果は、次の通りである。重量平均分子量： 13600（標準ポリスチレン換算）。

【0107】分散度： 1.52。

IR (KRS-5, cm^{-1}): 2960, 1727, 1259, 1148。

例 8

メタクリル酸(土)ーメバロニックラクトンエステル／
メタクリル酸アダマンチル共重合体の合成

テフロン™ コーティングされたスターラバーを入れた十分に乾燥させた200mlのナス形フラスコに、10g

(50.5ミリモル)の前記例1で調製のメタクリル酸

(土)ーメバロニックラクトンエステル、11.13g

(50.5ミリモル)のメタクリル酸アダマンチル、3

3.7mlのジオキサン及び2.49g(15.2ミリモル)

のアゾビスイソブチロニトリル(AIBN)を添加

し、窒素雰囲気下に80℃で8時間攪拌した。反応溶液

をテトラヒドロフラン(THF)で希釈した後、少量の

ヒドロキノンを含む3リットルの水-エタノール混合溶

液に滴下した。生成した沈殿をガラスフィルターでろ別

し、0.1mmHg及び45℃で16時間乾燥させた。得ら

れた白色の粉末を再びTHFに溶解させ、上記したもの

と同じ沈殿-乾燥作業を2度繰り返した。目的とする白

色の共重合体を得られた。収量=15.85g(75

%)。

【0108】 ^1H NMRから、得られた共重合体の共
重合比は1:1であることが判明した。この共重合体の
波長248nmにおける透過率は、95%(膜厚1 μm 、
石英基板上)であり、透明性に優れていることを示し
た。また、その他の分析の結果は、次の通りである。

重量平均分子量： 14100(標準ポリスチレン換
算)。

【0109】分散度： 1.41。

IR (KRS-5, cm^{-1}): 2912, 1722, 1259, 1093。

例 9

レジストパターンの形成

前記例7において合成した共重合体を乳酸エチルに溶解
して17重量%溶液とした。得られた乳酸エチル溶液

に、共重合体に対して5重量%の量のトリフェニルスル
ホニウムトリフルオロメタンスルホネートを加えて十分

に溶解させた。得られたレジスト溶液を0.2 μm のテ
フロン™ メンブランフィルタで濾過した後、HMD S 処

理を施したシリコン基板上に2000rpmでスピニング
コートし、120℃で60秒間プリベークした。膜厚0.7

μm のレジスト皮膜が得られた。このレジスト皮膜をK
r Fエキシマレーザステッパ(NA=0.45)で露光

した後、2.38%のテトラメチルアンモニウムハイド
ロオキシド(TMAH)水溶液で現像し、脱イオン水で

60秒間リンスした。38mJ/cm²の露光量で、0.3
 μm L/Sパターンが解像できた。

例 10

レジストパターンの形成

前記例8において合成した共重合体を乳酸エチルに溶解
して17重量%溶液とした。得られた乳酸エチル溶液

に、共重合体に対して5重量%の量のトリフェニルスル
ホニウムトリフルオロメタンスルホネートを加えて十分

に溶解させた。得られたレジスト溶液を0.2 μm のテ
フロン™ メンブランフィルタで濾過した後、HMD S 処

理を施したシリコン基板上に2000rpmでスピニング
コートし、120℃で60秒間プリベークした。膜厚0.7

μm のレジスト皮膜が得られた。このレジスト皮膜をK
r Fエキシマレーザステッパ(NA=0.45)で露光

した後、100℃で60秒間ベークし、2.38%のテ
トラメチルアンモニウムハイドロオキシド(TMAH)

水溶液で現像し、脱イオン水で60秒間リンスした。3
0mJ/cm²の露光量で、0.3 μm L/Sパターンが

解像できた。

例 11

レジストパターンの形成

前記例7において合成した共重合体を乳酸エチルに溶解
して17重量%溶液とした。得られた乳酸エチル溶液

に、共重合体に対して2重量%の量のトリフェニルスル
ホニウムトリフルオロメタンスルホネートを加えて十分

に溶解させた。得られたレジスト溶液を0.2 μm のテ
フロン™ メンブランフィルタで濾過した後、HMD S 処

理を施したシリコン基板上に2000rpmでスピニング
コートし、120℃で60秒間プリベークした。膜厚0.7

μm のレジスト皮膜が得られた。このレジスト皮膜をK
r Fエキシマレーザステッパ(NA=0.45)で露光

した後、100℃で60秒間ベークし、2.38%のテ
トラメチルアンモニウムハイドロオキシド(TMAH)

水溶液で現像し、脱イオン水で60秒間リンスした。2
0mJ/cm²の露光量で、0.3 μm L/Sパターンが

解像できた。

例 12

レジストパターンの形成

前記例8において合成した共重合体を乳酸エチルに溶解
して17重量%溶液とした。得られた乳酸エチル溶液

に、共重合体に対して2重量%の量のトリフェニルスル
ホニウムトリフルオロメタンスルホネートを加えて十分

に溶解させた。得られたレジスト溶液を0.2 μm のテ
フロン™ メンブランフィルタで濾過した後、HMD S 処

理を施したシリコン基板上に2000rpmでスピニング
コートし、120℃で60秒間プリベークした。膜厚0.7

μm のレジスト皮膜が得られた。このレジスト皮膜をK
r Fエキシマレーザステッパ(NA=0.45)で露光

した後、100℃で60秒間ベークし、2.38%のテ
トラメチルアンモニウムハイドロオキシド(TMAH)

水溶液で現像し、脱イオン水で60秒間リンスした。2
3mJ/cm²の露光量で、0.3 μm L/Sパターンが

例 13

メタクリル酸（±）ーメバロニックラクトンエステル／メタクリル酸 2-メチル-2-アダマンチル共重合体の合成

テフロン™ コーティングされたスターラバーを入れた十分に乾燥させた 100ml のナス形フラスコに、4.96g（25ミリモル）の前記例 1 で調製のメタクリル酸（±）ーメバロニックラクトンエステル、5.87g（25ミリモル）のメタクリル酸 2-メチル-2-アダマンチル、16.7ml のジオキサン及び 1.23g（9ミリモル）のアゾビスイソブチロニトリル（AIBN）を添加し、窒素雰囲気下で 80℃ で 8 時間攪拌した。反応溶液をテトラヒドロフラン（THF）で希釈した後、少量のヒドロキノンを含む 1 リットルのメタノールに滴下した。生成した沈殿をガラスフィルターでろ別し、0.1mmHg 及び 45℃ で 16 時間乾燥させた。得られた白色の粉末を再び THF に溶解させ、上記したものと同じ沈殿～乾燥作業を 2 度繰り返した。目的とする白色の共重合体粉末が得られた。収量＝7.44g（68.7%）。

【0110】¹H NMR から、得られた共重合体の共重合比はラクトン：アダマンチル＝46.5：53.5 であることが判明した。この共重合体の波長 248nm における透過率は 96%、そして 193nm では 64%（膜厚 1μm、石英基板上）であり、透明性に優れていることを示した。また、その他の分析の結果は、次の通りである。

【0111】重量平均分子量：13900（標準ポリスチレン換算）。

分散度：1.78。

IR（KRS-5, cm⁻¹）：2914, 1724, 1259, 1147, 1103。

供試レジスト	エッチングレート（Å/分）	レート比
NPR-820	523	1.00
PMMA	790	1.51
MLMA-MAdMA	610	1.17

上記の表に示した結果から、本発明によるレジスト（MLMA-MAdMA）のエッチング耐性は、ノボラックレジストである長瀬ポジティブレジスト NPR-820 のそれと同等であり、また、PMMA（ポリメチルメタクリレート）より格段に優れていることが確認された。

例 15

レジストパターンの形成

前記例 13 において合成した共重合体を乳酸エチルに溶解して 18 重量% 溶液とした。得られた乳酸エチル溶液に、共重合体に対して 5 重量% の量のトリフェニルスルホニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を 0.2μm のテフロン™ メンブランフィルタで濾過した後、HMDS 処理を施したシリコン基板上に 2000rpm でスピコートし、120℃ で 60 秒間プリベークした。膜厚 0.7

例 14

レジストパターンの形成

前記例 13 において合成した共重合体をプロピレングリコールメチルエーテルアセートに溶解して 19 重量% 溶液とした。なお、この共重合体溶液には、補助溶媒として、8 重量% の γ-ブチロラクトンも含ませた。得られた溶液に、共重合体に対して 5 重量% の量のトリフェニルスルホニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を 0.2μm のテフロン™ メンブランフィルタで濾過した後、HMDS 処理を施したシリコン基板上に 2000rpm でスピコートし、120℃ で 60 秒間プリベークした。膜厚 0.7μm のレジスト皮膜が得られた。このレジスト皮膜を KrF エキシマレーザステッパ（NA＝0.45）で露光した後、100℃ で 60 秒間ベークし、2.38% のテトラメチルアンモニウムハイドロオキシド（TMAH）水溶液で現像し、脱イオン水で 60 秒間リンスした。8.3mJ/cm² の露光量で、0.25μm ライン・アンド・スペース（L/S）パターンが解像できた。

【0112】次いで、上記のようにしてレジスト（MLMA-MAdMA）を塗布したシリコン基板を平行平板型 RIE 装置に収容し、Pμ＝200W、圧力＝0.02Torr、CF₄ ガス＝100sccm の条件下で 5 分間にわたってエッチングを行った。エッチングレート及びレート比（NPR-820 に対して）に関して、次の表に示すような試験結果が得られた。

【0113】また、比較のため、市販のノボラックレジストである長瀬ポジティブレジスト NPR-820（長瀬産業社製）及び PMMA（ポリメチルメタクリレート）を用いて同様なエッチング及び試験を行った。

μm のレジスト皮膜が得られた。このレジスト皮膜を KrF エキシマレーザステッパ（NA＝0.45）で露光した後、100℃ で 60 秒間ベークし、2.38% のテトラメチルアンモニウムハイドロオキシド（TMAH）水溶液で現像し、脱イオン水で 60 秒間リンスした。7.4mJ/cm² の露光量で、0.25μm L/S パターンが解像できた。

【0114】次いで、上記のようにしてレジストを塗布したシリコン基板を前記例 14 と同様な手法によってエッチングしたところ、長瀬ポジティブレジスト NPR-820（前出）と同等でありかつ PMMA よりも格段に優れたエッチング耐性を示すことが確認された。

例 16

レジストパターンの形成

前記例 13 において合成した共重合体を乳酸エチルに溶

解して 18 重量% 溶液とした。得られた乳酸エチル溶液に、共重合体に対して 2 重量% の量のジフェニルヨードニウムトリフルオロメタンスルホネートを加えて十分に溶解させた。得られたレジスト溶液を $0.2\ \mu\text{m}$ のテフロン™ メンブランフィルタで濾過した後、HMDS 処理を施したシリコン基板上に 2000rpm でスピンコートし、120℃ で 60 秒間プリベークした。膜厚 $0.7\ \mu\text{m}$ のレジスト皮膜が得られた。このレジスト皮膜を ArF エキシマレーザ露光装置（ニコン社製、NA=0.55）で露光した後、100℃ で 60 秒間ベークし、2.38% のテトラメチルアンモニウムハイドロオキシド（TMAH）水溶液で現像し、脱イオン水で 60 秒間リンスした。 $6\text{mJ}/\text{cm}^2$ の露光量で、 $0.2\ \mu\text{m}$ L/S パターンが解像できた。

【0115】次いで、上記のようにしてレジストを塗布したシリコン基板を前記例 14 と同様な手法によってエッチングしたところ、長瀬ポジティブレジスト NPR-820（前出）と同等でありかつ PMMA よりも格段に優れたエッチング耐性を示すことが確認された。

【0116】

【発明の効果】本発明によるレジスト組成物を使用すると、実用可能な感度で、膨潤のない微細なポジティブレ

ジストパターンを形成できる。また、このレジスト組成物の酸感応性重合体を共重合体の形とするとともに、その第 1 のモノマー単位のモノマー骨格を選択し、かつその共重合の相手として、複数個あるいは多環の脂環式炭化水素基を含有するようなモノマー単位を用いることにより、ArF エキシマレーザのような極短波長の露光光源にも対応可能な新規な高感度レジストを提供できる。

【0117】さらにまた、共重合体の形の酸感応性重合体において、第 1 のモノマー単位の側鎖に第 1 の保護基（エステル基）含有カルボキシル基を含ませることに加えて、第 2 のモノマー単位にもその側鎖に第 2 の保護基（エステル基）含有カルボキシル基を含ませた場合、カルボキシル基を保護している第 1 及び第 2 のエステル基の両方が酸触媒反応によって脱離可能であるため、従来のレジスト組成物の場合よりも高い感度及び高い解像性を容易に得ることができる。この共重合体も、その共重合体の第 2 のモノマー単位が多環の脂環式炭化水素基であるアダマンチル基を有するため、RIE 耐性が高くかつ、その共重合体自体には深紫外領域に大きな吸光係数を有する発色団を含まないため、ArF エキシマレーザのような極短波長の露光光源にも対応可能な新規な高感度レジストを提供できる。

フロントページの続き

(72)発明者 渡部 慶二
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内
(72)発明者 並木 崇久
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内
(72)発明者 五十嵐 美和
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内

(72)発明者 倉光 庸子
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内
(72)発明者 武智 敏
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内
(72)発明者 小太刀 明子
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内
(72)発明者 高橋 真
神奈川県川崎市中原区上小田中1015番地
富士通株式会社内

**This Page is Inserted by IFW Indexing and Scanning
Operations and is not part of the Official Record**

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: _____

IMAGES ARE BEST AVAILABLE COPY.

As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.